

VTT Technical Research Centre of Finland

New technologies for gas combustion emissions

Lehtoranta, Kati; Murtonen, Timo; Vesala, Hannu; Koponen, Päivi; Piimäkorpi, Pekka; Isotalo, Mia; Alanen, Jenni; Kuittinen, Niina; Rönkkö, Topi; Saarikoski, Sanna

Published: 29/04/2019

Document Version
Publisher's final version

[Link to publication](#)

Please cite the original version:

Lehtoranta, K., Murtonen, T., Vesala, H., Koponen, P., Piimäkorpi, P., Isotalo, M., Alanen, J., Kuittinen, N., Rönkkö, T., & Saarikoski, S. (2019). *New technologies for gas combustion emissions: Final report*. VTT Technical Research Centre of Finland. VTT Research Report No. VTT-R-00482-19



VTT
<http://www.vtt.fi>
P.O. box 1000FI-02044 VTT
Finland

By using VTT's Research Information Portal you are bound by the following Terms & Conditions.

I have read and I understand the following statement:

This document is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of this document is not permitted, except duplication for research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered for sale.



New technologies for gas combustion emissions - Final report

Authors:

Kati Lehtoranta, Timo Murtonen, Hannu Vesala, Päivi Koponen, Pekka Piimäkorpi

VTT Technical Research Centre of Finland

Mia Isotalo, Jenni Alanen, Niina Kuittinen, Topi Rönkkö

Tampere University

Sanna Saarikoski

Finnish Meteorological Institute

Confidentiality:

{Public}

Report's title New technologies for gas combustion emissions - Final report								
Customer, contact person, address		Order reference						
Project name New technologies for gas combustion emissions		Project number/Short name NewGas						
Author(s) Lehtoranta et al.		Pages 27/40						
Keywords		Report identification code VTT-R-00482-19						
Summary <p>The NewGas project focuses on characterization of gas combustion emissions. The project studies the effect of the combustion process, fuel, lubricating oil and catalysts on the emission formation. In addition, different emission measurement methods are studied. The earlier developed gas engine research facility was modified to be suitable for studies. Studies with natural gas and propane, as well as with two different lubrication oils and catalysts were done utilizing this facility. The exhaust hydrocarbon (HC) composition was found to be different from propane fuel compared to methane fuel (i.e. natural gas, NG) and no methane was found from the exhaust when using propane as fuel while ethylene, propene and propane were found. The particle mass emissions were low and total particulate matter (PM) resulted to same level with propane and NG fuels. However, remarkable differences were seen in particle number concentrations between fuels. For propane, nanoparticle emissions were significantly smaller than for natural gas. The change of lubricating oil was found to have some effect on the particle emission also.</p> <p>High NO_x reductions were observed when using selective catalytic reduction, although the level was not as high with propane fuel as was earlier observed in the case of natural gas fuel. The oxidation catalyst with higher activity was found to decrease also propane emissions and the emissions of particulate matter total mass. However, a catalyst combined with high exhaust temperatures increased nanoparticle number concentrations.</p> <p>In this project, experimental field studies on gas combustion emissions were conducted at biogas and burner combustion facilities. The NO_x, CO, methane and formaldehyde concentrations in the biogas engine exhaust were found to be relatively similar to what was measured on the research facility. This indicates that the catalyst studies done at research facility would be relevant also to this real application case utilizing biogas as fuel.</p> <p>The results from the burner studies indicated that the NO_x, CO and HC concentrations were all very low when measured downstream of the burner only.</p>								
Confidentiality	{Public}							
Espoo 29.4.2019 <table border="0"> <tr> <td>Written by</td> <td>Reviewed by</td> <td>Accepted by</td> </tr> <tr> <td>Kati Lehtoranta, Senior Scientist</td> <td>Timo Murtonen, Senior Scientist</td> <td>Jukka Lehtomäki, Research Team Leader</td> </tr> </table>			Written by	Reviewed by	Accepted by	Kati Lehtoranta, Senior Scientist	Timo Murtonen, Senior Scientist	Jukka Lehtomäki, Research Team Leader
Written by	Reviewed by	Accepted by						
Kati Lehtoranta, Senior Scientist	Timo Murtonen, Senior Scientist	Jukka Lehtomäki, Research Team Leader						
VTT's contact address P.O.Box 1000, FI-02044 VTT								
Distribution (customer and VTT) NewGas project partners and Business Finland, in addition distribution through VTT's publication database.								
<i>The use of the name of VTT Technical Research Centre of Finland Ltd in advertising or publishing of a part of this report is only permissible with written authorisation from VTT Technical Research Centre of Finland Ltd.</i>								

Contents

Contents.....	2
1. Introduction.....	3
2. Project target	4
3. Emission measurement setup	4
4. Measurement methods study – focus on particles.....	5
4.1 Nanoparticle formation mechanisms.....	5
4.2 EPA 5 + EPA 202	8
5. Field study for biogas combustion emissions	8
6. Field study for burner combustion emissions	14
7. Emission characterization and reduction study using the gas engine research facility.....	16
7.1 Results of lubricating oil studies with NG fuel.....	18
7.2 Results of propane fuel studies.....	20
7.3 Results of catalyst studies	21
8. Workshop.....	25
9. Conclusions	25
10. Publications of the project.....	26
11. References of literature outside project.....	27
Appendixes	27

1. Introduction

Climatic and environmental issues form currently major problems for mankind and societies around the world (Lelieveld et al., 2015; IPCC 2013). These problems challenge globally the societies and businesses to increase the research and development of sustainable and environmentally friendly technologies, products and courses of action. As a result, the solving of problems may offer very significant opportunities for new business in the areas of cleantech, bioeconomy and circular economy.

Natural gas (NG) is already an important fuel in energy production and its utilization is increasing. At the same time, also other gaseous fuels are applicable. While NG is primarily composed of methane, the use of other gases like ethane and propane is expected to increase. In addition, biogas can be produced from raw materials such as agricultural waste, municipal waste, sewage or food waste. Since biogas is a renewable energy source it is more and more relevant to be utilized, solely or mixed with natural gas. This growing trend in the usage of gas and biogas as energy sources enhances the sustainable use of natural resources and can significantly help to lower the CO₂ emissions but this should not compromise the environmental protection or the human health. Recent research results show that compounds like methane (strong greenhouse gas), formaldehyde (toxic), CO (toxic, indirect greenhouse gas), NO_x (health and environmental effects) and particles (health and environmental effects) are found from the exhaust of a natural gas engine (Alanen et al. 2015; Lehtoranta et al. 2016). The changing of gas composition likely changes the emissions of gas combustion processes, power plants and vehicles, and produces new requirements for emission reduction and emission measurements. Especially with biogases also the purity is a challenge, causing increased need for new gas purification technologies (e.g. for impurities like siloxane) (Kajolinna et al. 2015).

The emission profile of gas engines and power plants using gas has been observed to be significantly different when compared to other pollutant sources. In general, the use of gas in combustion applications has been recognized to be a potential way to decrease the atmospheric emissions when compared e.g. to liquid fossil fuels. However, recent studies have shown that e.g. the particle emissions of gas combustion applications can contain large number of nanoparticles, being smaller than 10 nm in diameter (Alanen et al. 2015). This will also set new requirements for emission measurements, especially for nanoparticle measurements and exhaust sampling procedures. E.g. the understanding on the basis of the measurement standards and their correlation with real world emissions in gas combustion research is challenging, which affects even the development of new engine and exhaust aftertreatment technologies. However, challenging characteristics of gas engine emissions together with enhanced scientific knowledge opens new possibilities for new measurement device development and for emission reduction technique development.

The Finnish industry dealing with gas emissions, now and in the near future, consists of engine and boiler manufacturers, natural gas and biogas industry, fuel and oil industry, burners and combustion systems developers, energy production plants, exhaust after-treatment manufacturers and ship owners. Finnish industry focusing on emission measurements and control techniques is in a key role, as the emissions from gas combustion open new measurement needs and possibilities.

In this project, we conducted comprehensive gaseous and particle emissions studies for NG and propane combustion exhaust. We studied the role of lubricating oil on the emission formation. In addition, the effect of catalyst systems on the exhaust gas composition utilizing several measurement methods and instruments was studied. Experiments were conducted in laboratory and in real applications. The real application experiments included burner combustion emissions study and study on biogas engine emissions.

Project partners were: VTT Technical Research Centre of Finland, Tampere University and Finnish Meteorological Institute. In addition, company partners were Airmodus, Dekati, Dinex Ecocat, Neste, Oilon and Wärtsilä.

2. Project target

The objectives of the NewGas project were:

- To study and develop the measurement methods, sampling systems and measurement devices suitable for measurements of the gas combustion emissions, especially particulate emissions
- To conduct experimental field studies on gas combustion (burner combustion, biogas combustion)
- To study the emission formation process and emission reduction possibilities focusing in propane fuel gas in addition to natural gas
- To explore new solutions for emission mitigation

3. Emission measurement setup

We present here the basics of the emission measurement setup, utilized in the different measurement campaigns (at TUT laboratory, VTT laboratory and when studying biogas and burner combustion emissions) with minor variations.

The gaseous emission measurement setup consisted of a chemiluminescence detector (CLD), used to measure the NO_x (NO , NO_2), a non-dispersive infrared (NDIR) analyser to measure CO and CO_2 , and paramagnetic method for O_2 Horiba PG-250 analyser and Ecophysics 700 ELht heated chemiluminescence analyser (HCLD) were utilized. Gasmeter DX-4000 fourier transformation infrared (FTIR) was used for measuring multiple gaseous compounds (e.g. water, methane, formaldehyde). The FTIR as well as the sampling line and the filter prior to the FTIR spectrometer were heated to 180 °C. In addition, methane, ethane, propane and ethylene components were measured with a gas chromatograph (GC). Hewlett Packard 5890A Series II gas chromatograph (GC) was used and the dried exhaust gas samples for the gas chromatograph were collected in Tedlar® bags. In addition, an online gas chromatograph (Agilent Micro GC) was applied for measurements. The sample for aldehyde measurement was diluted utilizing the same system utilized for particulate mass measurement. Samples were collected by using the DNPH (dinitrophenyl hydrazine) cartridges. In the cartridges, aldehydes form hydrazine derivatives which are then analysed by high performance liquid chromatography. The DNPH derivatives were extracted with an acetonitrile, and the extraction was diluted with water (1:1) and analysed with the HPLC-technology (Agilent 1260, UV detector, Nova-Pak C18 column).

In this project, the particle emission characterization was made relatively comprehensively. Typically the measurement consisted of standardized particulate matter (PM) measurement and more detailed measurements to characterize particles in the primary exhaust, fresh exhaust and aged exhaust. Here primary exhaust particles refer to the particles that are formed in high temperature and exist already before the dilution and cooling of exhaust. Fresh exhaust indicates the exhaust immediately after the cooling and dilution, thus the particulate matter of fresh exhaust can contain also semivolatile compounds i.e. compounds that are in gaseous phase in primary exhaust. In this project, we used a specific exhaust sampling and dilution system to study the fresh exhaust characteristics. This system has been previously seen to mimic the real-world formation of fresh exhaust particle characteristics, especially in respect of particle size distribution and nucleation mode particle

formation. The term “aged exhaust” refers to the processes that modify the exhaust aerosol in the atmosphere during several days after the emission. In this study, a potential aerosol mass (PAM) chamber was used to simulate the aging process of the exhaust in the atmosphere (secondary particles). In the PAM, an oxidative environment was produced by two UV lamps emitting 185 nm and 254 nm radiation in a small (13 l) flow-through chamber.

PM was measured with a sampling according to international standard ISO 8178-1:2006. According to this standard the PM is measured as any material collected on a filter after diluting exhaust gas with clean, filtered air to a temperature higher than 42 °C and less than or equal to 52 °C, as measured at a point immediately upstream of the filter. A dilution ratio of 10 and a sampling time of 30 minutes were used. Samples were collected on TX40HI20-WW filters.

In real-time particle studies, gas combustion emission was characterised by measuring the particle number concentration, particle number size distribution and chemical composition of the exhaust particles. Particle number size distributions were usually measured using scanning mobility particle sizers (Nano-SMPS and Long-SMPS, TSI Inc.) and electrical low pressure impactor (ELPI, Dekati Ltd.). Particle number concentrations were measured using several condensation particle counters (CPC, TSI Inc. and Airmodus Ltd.) with different cut-points (1.3–10 nm) and particle size magnifier (PSM, Airmodus Ltd.). The chemical composition of PM₁ particles (particles with diameter < 1 µm) was measured by using a soot particle aerosol mass spectrometer (SP-AMS, Aerodyne Research Inc., USA). The SP-AMS is a combination of two instruments: an Aerodyne high-resolution time-of-flight aerosol mass spectrometer and a single-particle soot photometer (SP2; Droplet Measurement Technologies, CO, USA). SP-AMS is capable of measuring refractory material (black carbon, metals) and non-refractory material (organic matter, sulfate, nitrate, ammonium, chloride) in particles. Volatility studies for exhaust particles were usually conducted using a thermodenuder (TD).

4. Measurement methods study – focus on particles

4.1 Nanoparticle formation mechanisms

Measuring nanoparticles is extremely challenging due to the lack of suitable measurement devices, sampling losses and phenomena like gas-to-particle conversion causing new particle formation. In this project, the formation mechanisms of nanoparticles were studied by varying catalyst temperature and the composition of exhaust. Targeted exhaust composition was a simplified diesel exhaust or e.g. NG engine exhaust with very little soot formation. The exhaust was generated with an SO₂ (3% SO₂ in N₂) injection (20 ml min⁻¹) in a N₂ (50 l min⁻¹) and air (50 l min⁻¹) flow that was led through a heated oxidation catalyst (oxicat). The exhaust composition was modified by increasing relative humidity (adding water) and by adding NH₃, NO, lubricant oil and soot in the flow together with the SO₂ injection. The soot particles were generated with a flat flame burner (acetylene as fuel) and mixed in with the exhaust flow in an ejector system (Dekati Ltd.).

The sampling and dilution was done with a porous tube diluter (PTD) with dilution ratio of ca. 12, followed by an ejector diluter with dilution ratio of ca. 10. A PAM oxidation flow reactor was used to imitate the atmospheric aging of the aerosol sample. An ELPI+, Nano- and Long-SMPS, and a SP-AMS were used to characterize the formed particulate matter.

In the first experiment, the oxidation catalyst was heated to 3–5 different temperatures between 235–344 °C enabling different SO₂ oxidation rates. Particle formation in fresh and aged exhaust in these varying oxidation catalyst temperatures is presented in Fig. 1. The

particulate formation in fresh exhaust depended strongly on the oxidat temperature. With the lowest oxidat temperatures, no sulfur-driven nucleation particles were formed. With the soot addition, the dependence of fresh particulate mass concentration on the oxidat temperature was also strong. Furthermore, the soot addition offered the sulfuric species a condensation sink and decreased the lowest oxidat temperature where sulfuric particle formation could happen. Nevertheless, the secondary particulate matter formation did not depend strongly on the oxidat temperature. In all the measured oxidation catalyst temperatures, with both exhaust compositions, the formed secondary particulate mass in aged exhaust was $0.8\text{--}1.5 \times 10^5 \mu\text{g m}^{-3}$.

Primary

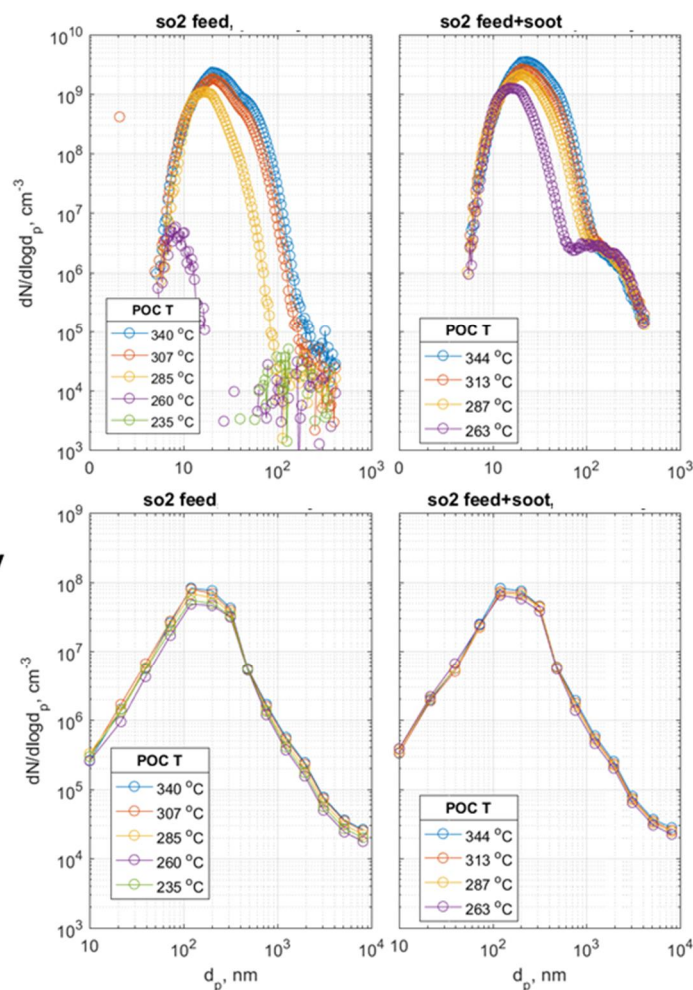


Figure 1 The number distributions of fresh exhaust and secondary particles in aged exhaust measured with the SMPS (assumed spherical particles with unit density). The concentrations have been corrected with the dilution ratios.

Same effect is demonstrated by showing the effects of oxidative exhaust after-treatment on the partitioning of sulfuric species (Fig. 2). The phase of the sulfuric species in freshly emitted exhaust depends on their oxidative state, i.e. for instance on the performance of the oxidation catalyst. Without the catalyst, sulfuric species are in gaseous form in the exhaust but when the catalyst is added, and especially when its temperature is increased, a larger fraction of sulfuric species is in particle phase. However, according to our aging study with the PAM, the sulfuric species end up finally in particulate phase in the atmosphere almost independent on the oxidative catalyst exhaust after-treatment.

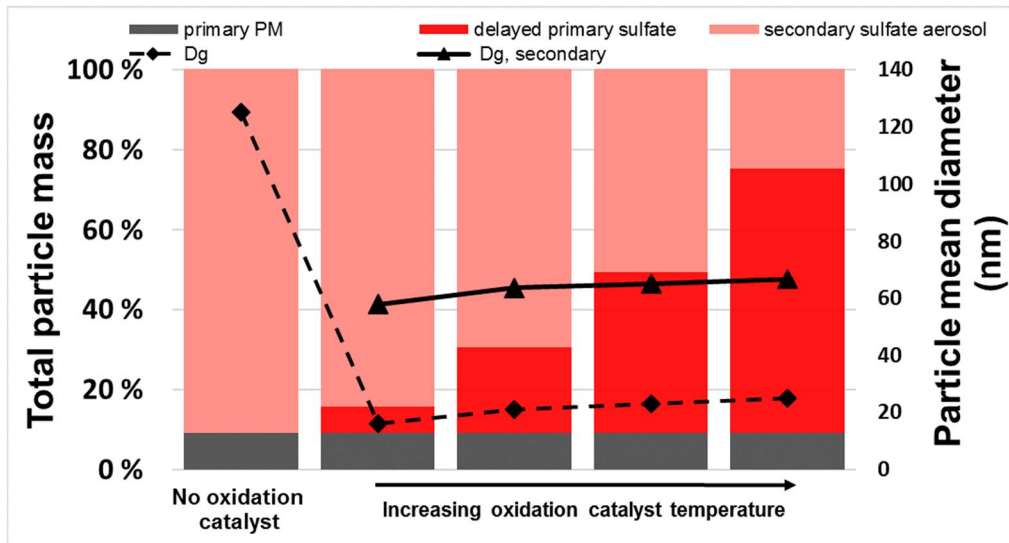
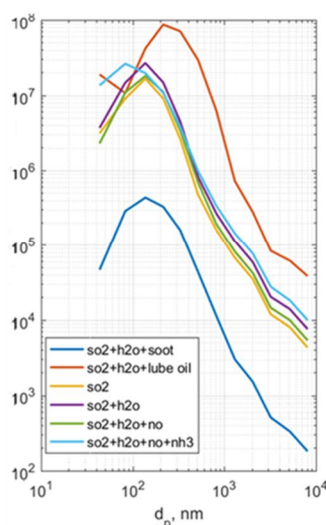


Figure 2 The effects of oxidation catalyst on the partitioning of sulfuric compounds in exhaust aerosol. Delayed primary sulfate refers here for the formation of sulfate in fresh exhaust.

In the second experiment, the impact of water, soot, NO, NH₃ and lubricant oil on secondary particle number and mass size distributions was investigated. In terms of number size distributions, adding water did not change the distribution but adding water and soot decreased particle number significantly (Fig.3). In contrast, adding water, NH₃ and NO increased the number of particles < 10 nm whereas adding water and lubricating oil changed the maximum of particle number from ~150 nm to >200 nm and increased the total number of particles. Regarding the mass size distributions for the chemical species, only water+NO+NH₃ changed the mass size distribution. For that test condition, there was a mode for ammonium and nitrate at slightly smaller size (at ~130 nm) than that for sulfate (at ~150 nm).

Number size distribution



Chemical composition

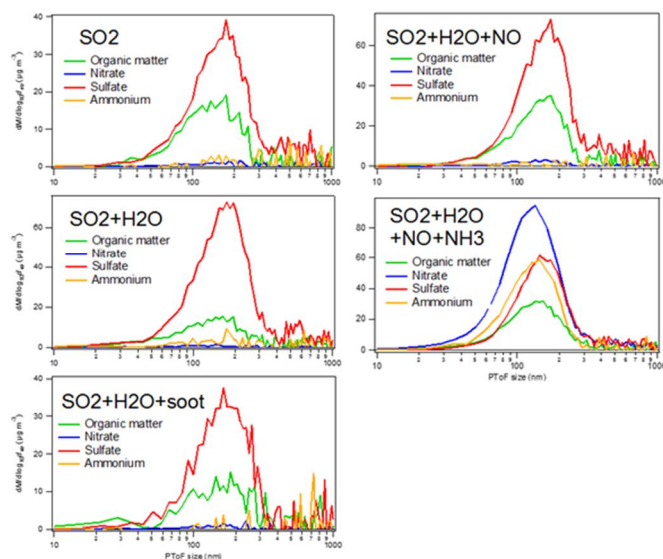


Figure 3 The impact of water, soot, NO, NH₃ and lubricant oil on secondary particles.

4.2 EPA 5 + EPA 202

The standard method of 'EPA 5 + EPA 202' was studied and adopted to measurements of task 5.

The EPA Method 5 is called 'Determination of Particulate Matter Emissions From Stationary Sources'. This results the filterable particulate matter (FPM). In this method particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 120 ± 14 °C. The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

The EPA Method 202 is called 'Dry Impinger Method for Determining Condensable Particulate Emissions From Stationary Sources'. This results the condensable particulate matter (CPM). The CPM is collected in dry impingers after filterable PM has been collected on a filter. The method includes procedures for measuring both organic and inorganic CPM.

The detailed description of the EPA 5 + EPA 202 procedure, with all the instruments and working phases is presented as an appendix (in Finnish). The results of the measurements done according to this method are presented together with the other results of Task 5.

5. Field study for biogas combustion emissions

The aim of the biogas combustion study was to produce information for biogas actors as well as for development of new catalysts, filters and measurement technologies. Biogas combustion measurements were conducted in Viikinmäki, which is the biggest wastewater treatment plant in Nordic countries, own by HSY (Helsinki Region Environmental Services Authority). The waste water treatment process in Viikinmäki is based on an activated sludge method. The organic matter in the sludge created during the wastewater treatment process is utilised by digesting the sludge. The biogas generated during this digestion process is recovered. With the help of energy produced with biogas, the plant reaches nearly complete self-sufficiency in electricity and heating.

Before the biogas is conducted to the power plant engines, it goes through an activated carbon filter to remove impurities like siloxanes. Four different engines are operating with biogas in Viikinmäki plant. In the present project, the emissions were measured from one of those engines (see Figure 4). An organic ranking cycle (ORC) -device was connected downstream of the engine to produce electricity from the waste heat. This device operated only on high engine loads. In addition to high loads, also lower loads were studied in the present project (but without the ORC operating).

An emission characterization of biogas combustion included studies on gaseous compounds like CO, NO_x, hydrocarbons (methane & non-methane) and aldehydes. However, the project group also conducted particle studies. In addition, the biogas composition was also measured with FTIR.

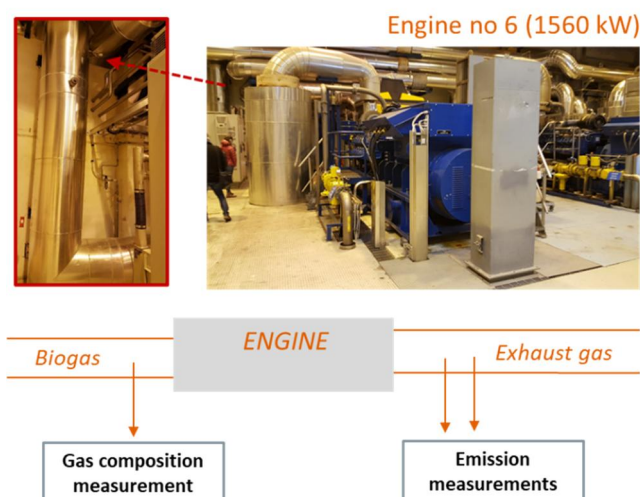


Figure 4 A schematic of the test setup, and a photo of the biogas engine and the measurement point.

The biogas composition results are presented in Table 1. No siloxanes were found from the biogas confirming that the activated carbon filters were working properly. For comparison, the natural gas composition is also added to the same table. The biogas was mainly formed of methane and carbon monoxide. In general, if the biogas is to mix with natural gas network, it is upgraded to fulfil the same standards as fossil natural gas. By the upgrading process, the methane in biogas is concentrated and this upgraded gas is called biomethane. However, in this case, at Viikinmäki, the biogas was directly utilized in an engine so there was no need for upgrading.

Table 1 Composition of natural gas and biogas. Natural gas composition measured from the gas line at VTT. Biogas composition measured downstream of activated carbon filters at Viikinmäki.

Gas composition	Natural Gas (VTT)	Biogas (Viikinmäki)
methane	97.2 %	61.4 %
ethane	1.37 %	-
propane	0.17 %	-
other hydrocarbons	0.07 %	-
nitrogen	0.9 %	0.31 %
carbon dioxide	0.2 %	38.7 %
oxygen	-	0.06 %
hydrogen	-	0.01 %

The NO_x, CO, methane and formaldehyde concentrations in the gas engine exhaust were found to be relatively similar to what was measured on VTT research facility from a smaller, passenger car engine exhaust (Fig. 5). This indicates that the catalyst studies done at VTT research facility would be relevant also to this real application case utilizing biogas as fuel in

a 1560 kW engine. The emission levels were found to depend on the engine loading, in the case of CO, methane and formaldehyde, higher levels were found at lower engine loads.

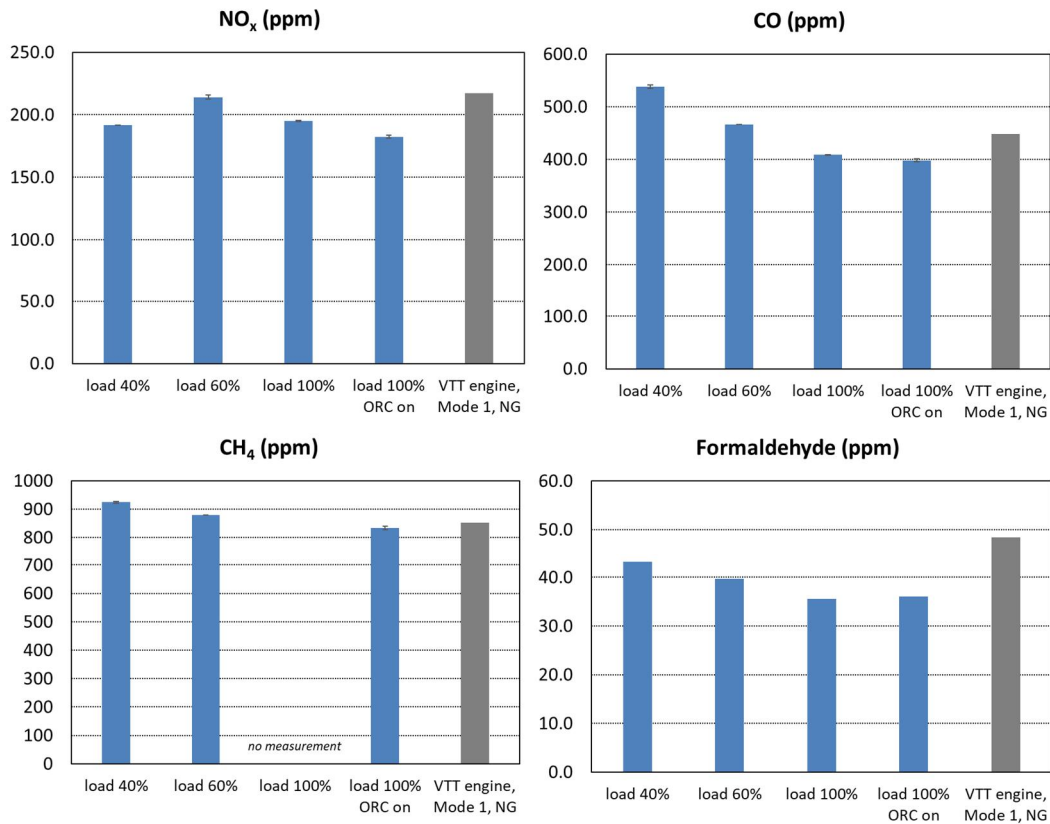


Figure 5 NO_x, CO, CH₄ and formaldehyde concentrations measured from biogas combustion at 40%, 60% and 100% engine loads with ORC off and 100% load with ORC on. For comparison, the emission concentrations from the smaller research engine run with natural gas are added to each chart with grey.

The PM measurements resulted to very low levels. Lowest level of 0.46 mg/m³ was recorded at highest engine load of 100% while the highest PM of 0.69 mg/m³ was found at the lowest engine load tested (i.e. 40% load). These PM values are the same level to the ones measured at smaller VTT engine with NG fuel.

Detailed particle measurements (measurement setup in appendix) for fresh exhaust showed that the sizes of exhaust particles were very small, and sub 10 nm particles dominated the particle number size distributions. In addition, thermodenuder studies indicated that most of the exhaust particles were volatile at temperature 265 °C, which is shown in Figure 6 with 60 % and 100 % engine load and without using the ORC system.

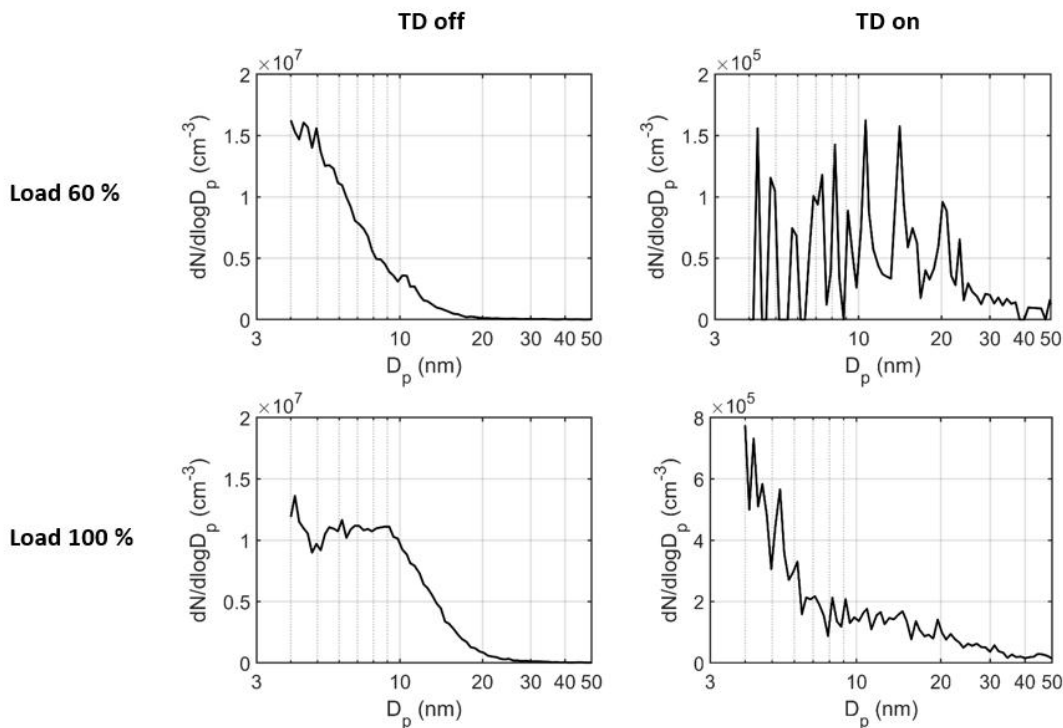


Figure 6 Particle size distributions measured by Nano-SMPS measured without TD (left-hand side) and with TD (right-hand side) using two different engine loads (60 % and 100 %). The detection limit for Nano-SMPS was ~3 nm. Notice also the difference in figures' y-axis scales.

Results also showed that particle number concentrations and size distributions were slightly affected by engine load conditions (Figure 6). Without TD, the mean particle size of exhaust particles was 6–8 nm at 100 % engine load while it was smaller than 5 nm at 60 % load. With the TD, the size distributions were significantly different; at 100 % load the size distribution consisted of two particle modes, one in particle sizes smaller than 6 nm and the other in particle sizes 8–20 nm, and only one mode at 60 % load. The bimodality of the particles size distribution at 100 % load is demonstrated by Figure 7, which shows the size distributions both with linear and logarithmic y-axis scales.

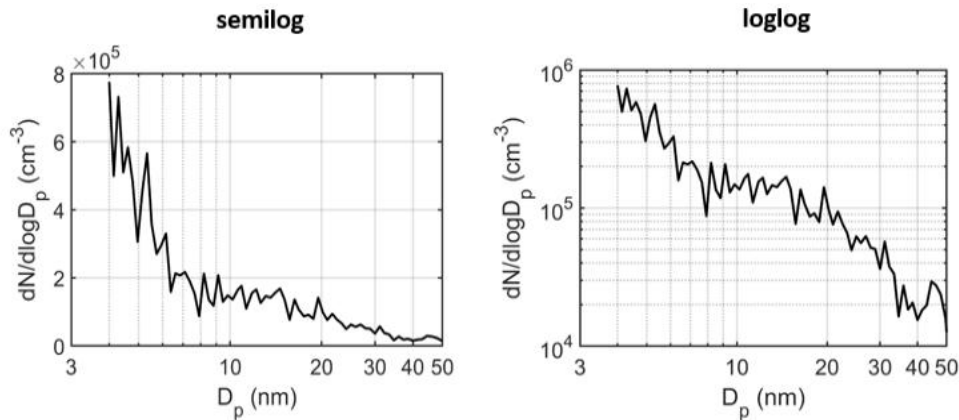


Figure 7 Number size distributions of non-volatile particles at 100 % load, without the ORC in exhaust line using linear y-axis scale (left-hand side) and logarithmic y-axis scale (right-hand side).

With 100 % engine load, using of the ORC system was observed to decrease exhaust particle number concentrations very effectively, even two orders of magnitude (Figure 8). When comparing the size distributions of figures 6 and 8, measurement results indicate that the ORC removes efficiently the semivolatile components of the exhaust; the particle concentration level with ORC was similar than the non-volatile particle concentration level without ORC.

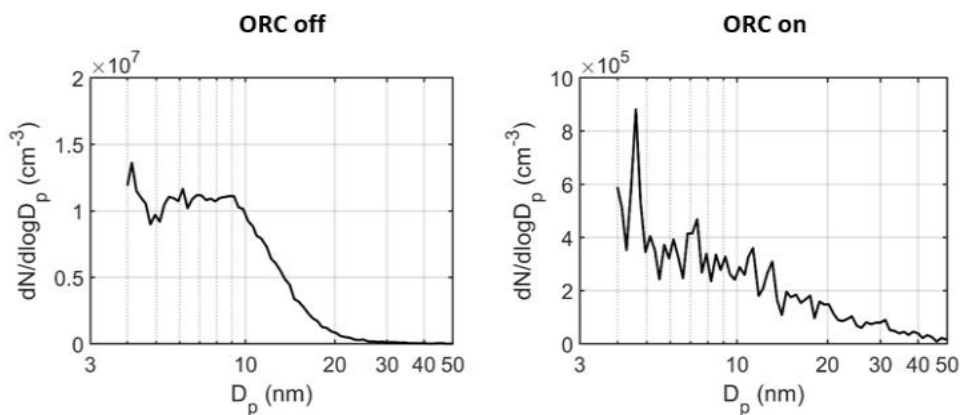


Figure 8 Particle size distributions measured by Nano-SMPS measured without ORC and with ORC in exhaust line. Measurement was conducted at 100 % engine load and without the TD.

The chemical composition of particles in the fresh exhaust from the biogas engine (without TD) is presented in Fig.9. 85–88% of particles consisted of organic matter and there was only a minor fraction of inorganic species (sulfate 6–7%, nitrate 4–5% and ammonium 2–3%). Based on the mass spectra, organic matter consisted mostly of hydrocarbons. Total mass of PM₁ particles, calculated by the sum of chemical species, was similar to all engine loads without the ORC while PM₁ was clearly smaller with ORC. Compared to the smaller VTT engine with NG fuel, PM₁ mass from biogas engine was almost five times smaller than PM₁ from the VTT engine.

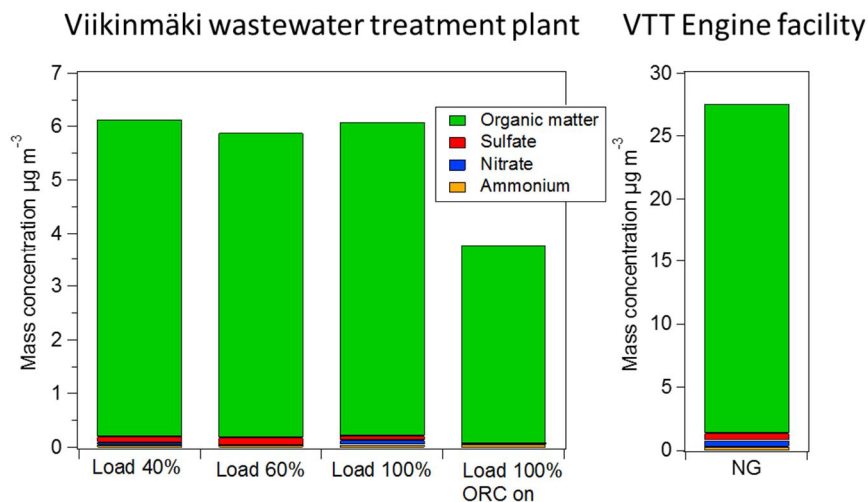


Figure 9 Chemical composition of PM₁ particles in fresh exhaust measured without TD at 40%, 60% and 100% engine loads with ORC off and 100% load with ORC on. For comparison, the composition from the smaller research engine run with natural gas at VTT is presented on right side.

The emissions of secondary particles, formed from the exhaust gases of biogas engine in the atmosphere, are shown in Fig. 10. Compared to the PM₁ emissions in fresh exhaust, the mass emissions of secondary particles were more than 100 times larger. Also the chemical composition of secondary particles was different from that of fresh particles as the mass contribution of sulfate was larger (especially with higher UV lamp voltage). Compared to the VTT engine with NG fuel, mass emission for secondary particles from biogas engine were at the same level. The most notable difference between secondary particles from biogas engine and VTT NG engine was that the composition of particles from VTT engine was dominated by sulfate.

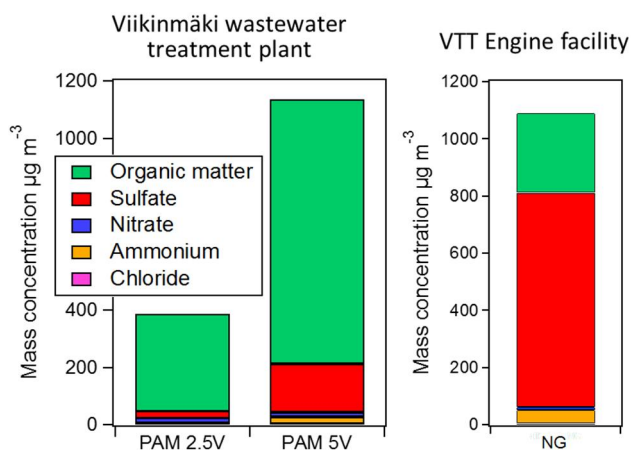


Figure 10 Chemical composition of secondary particles measured from biogas combustion at two UV lamp voltages. For comparison, the composition from the smaller research engine run with natural gas at VTT is presented on right side.

6. Field study for burner combustion emissions

Task 4 includes a burner combustion emissions study. In addition to engine emissions (studied in other tasks of this project), the target in this task was to produce information about one different combustion process emissions, their environmental influences and their reduction possibilities.

The burner combustion study was performed in-collaboration with Oilon at their facility. The study consisted of measurements of gaseous emissions like hydrocarbons and NO_x and relatively large set of measurements on exhaust particle characterization.

Measurements were done with a burner only and with a burner combined with a catalyst. Basics of the setup are shown in Figure 11. Emissions were measured upstream and downstream of a boiler. Two different power levels were tested with the burner, namely 40 kW and 27 kW while the tested levels with the burner and catalyst combination were 16 kW and 22 kW. Natural gas was utilized as a fuel.

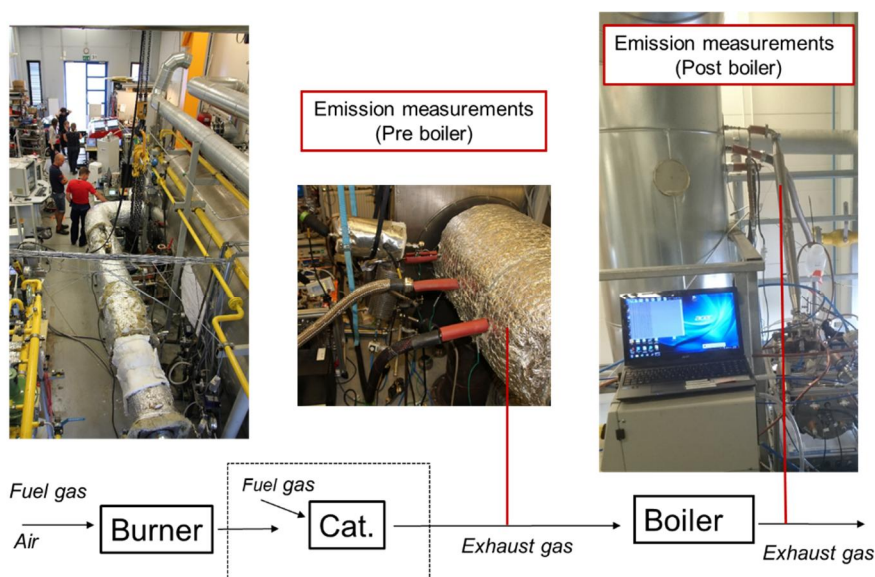


Figure 11 A schematic of the test setup and related photos at Oilon facilities.

The results indicated that the NO_x , CO and HC concentrations were all very low when measured downstream of the burner only. When applying the catalyst in combination with the burner, a small increase was observed in HC concentrations, namely in methane level, which was found to be 5-35 ppm while measured downstream of the burner only the methane level was below 5 ppm.

In general, during the measurement campaign, there were number of disturbances in the combustion process. The measurement results are discussed mainly only for the cases of stabile conditions i.e. without any disturbances. However, we note that the gaseous emissions results indicated that in the case of some disturbance the emissions levels of e.g. CO and methane rose quickly to very high levels.

The PM concentrations were found to be low in all cases studied. Some higher PM levels were measured downstream of the boiler. However, it should be noted that the boiler was oversized for the burner and that the boiler had some leakage. The leakage was not constant but changed from one case to another.

The particle number size distributions were found to be bi-modal when the burner was combined with the catalyst, suggesting that the fresh exhaust included both nucleation and

soot particles. In the measurements with only the thermal burner, the observed particle concentrations were reduced and the particles were smaller in size as shown in Figure 12. Larger particle mean diameters measured post-boiler (20-30 nm) than pre-boiler (5-10 nm) and drop in particle concentrations imply losses in the boiler region and growth of the particles by condensation and coagulation.

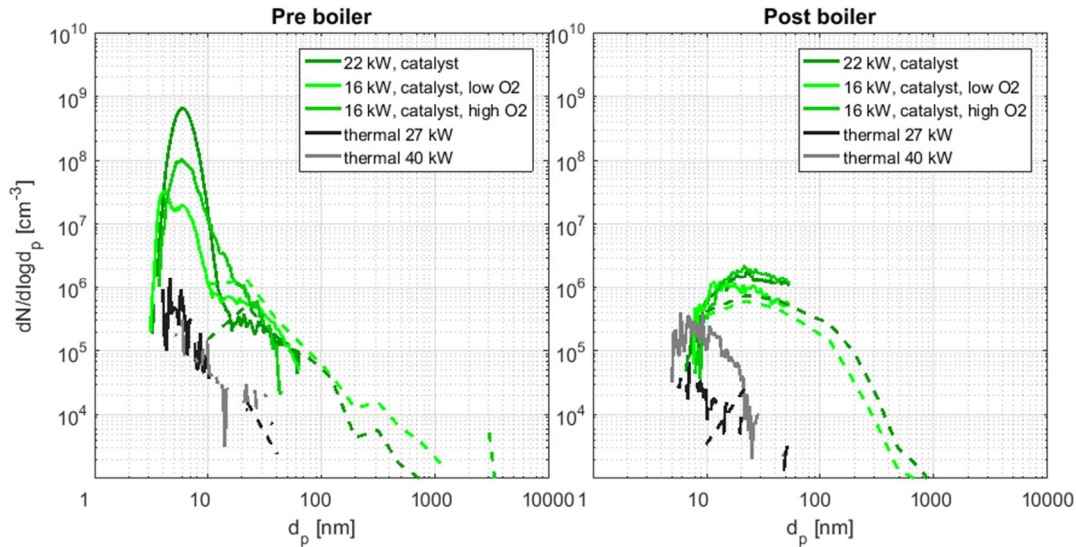


Figure 12 Particle number size distributions measured by Nano-SMPS (solid lines) and ELPI+ (dotted lines). Black lines denote measurements with burner only and green lines with burner combined with catalyst.

Measurements with several CPCs and PSM with different cut-points gave additional information of the particle concentrations in very small particle size range of 1-4 nm. As shown in Figure 13, majority of the particles could be seen in size class as small as 1-2.4 nm for the case of thermal burner alone and thermal burner combined with catalyst operating at low oxygen. Overall, 63-83% of the particles in all cases had diameters below 4 nm.

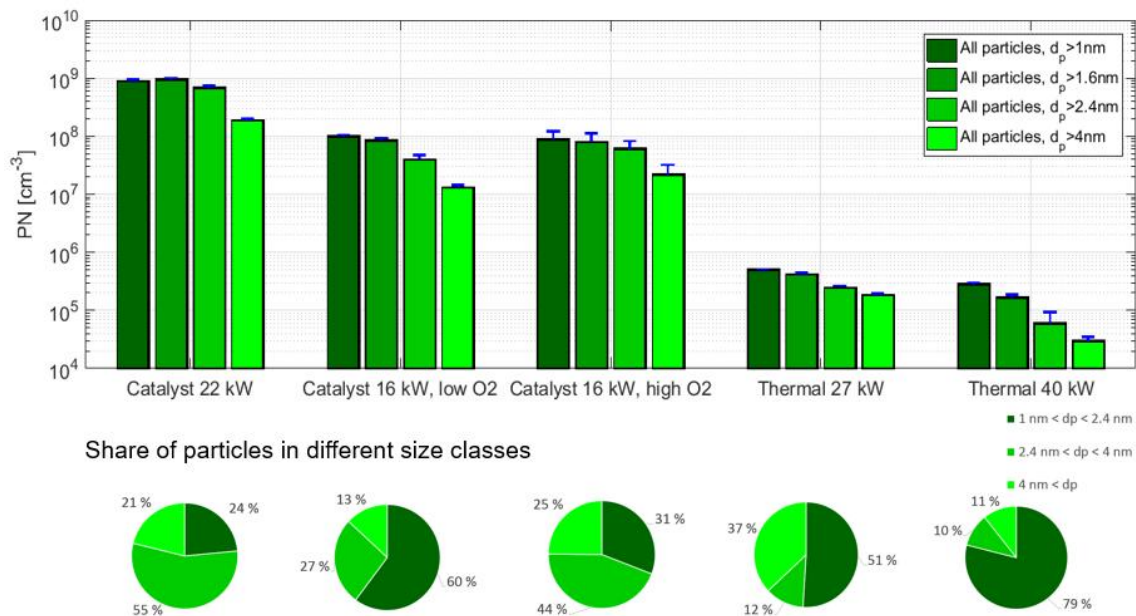


Figure 13 Particle concentrations before the boiler region measured by CPCs and PSM with different cut-off sizes. Comparison of the concentrations gives the shares of particles in different size classes.

Surprisingly large fraction of the particles were non-volatile at the temperature of 265 °C. In the case of thermal burner alone, nearly 100% of the particles remained after thermal treatment, and in the case of the thermal burner combined with catalyst, the non-volatile fraction was 23-55% of the particle number.

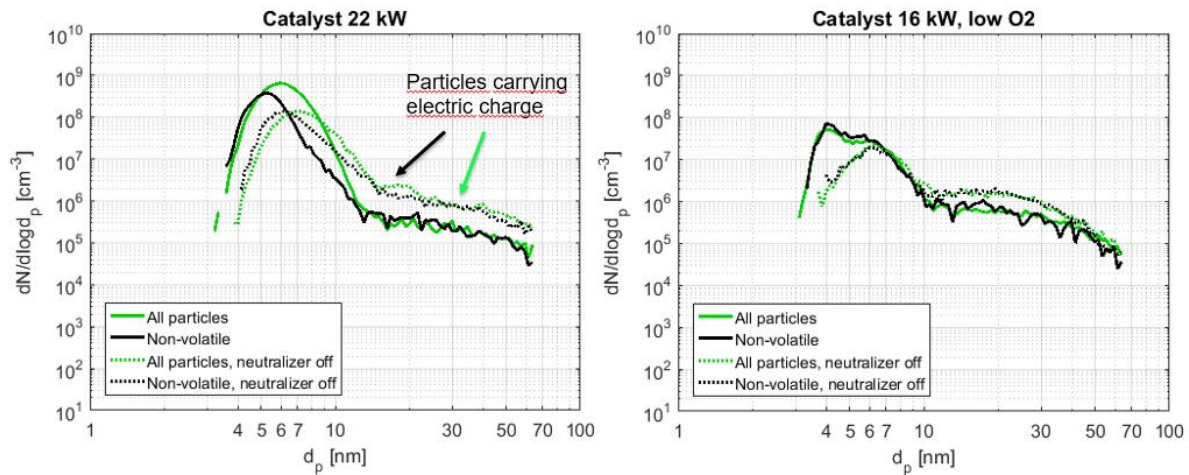


Figure 14 Number size distributions for all and non-volatile particles measured before the boiler. Dotted lines denote measurements during which the Nano-SMPS only sampled particles that carry electric charge.

In this study, also the charge state of the emitted particles was investigated. Results are shown in Figure 14 for the burner equipped with catalyst, in the case of thermal burner alone, concentrations were too low for the analysis to be made. It was found that the particles carried electrical charge because they were classified by the Nano-SMPS also without a diffusion charger (neutralizer). Comparing the size distributions of particles measured with and without the neutralizer, it could be seen that the soot mode particles were relatively more charged than the particles in the nucleation mode size range. Especially the charging of the nucleation mode particles indicates that the particles were born in high temperatures, most likely in the vicinity of the burner. Results related to particle charging state have been studied also in CENGE-project and presented earlier by Alanen et al. (2015).

7. Emission characterization and reduction study using the gas engine research facility

This task combined knowledge of all experts and state-of-the-art techniques, including techniques developed in companies own projects, into the same experiments.

First the gas engine research facility (Murtonen et al. 2016) was modified to be suitable to study new gas compositions (i.e. in this case the propane was selected). Updates were needed for the accurate injection of propane and for the measurement of fuel gas final composition. In addition, the engine needed to be readjusted for the new fuel gas. The engine parameter setup and operating points were selected to meet the real life application reference values. The reference values were based mainly on Wärtsilä's own results from their engines when operating with propane.

The propane that was utilized as a fuel was Neste's product Propane 95 with a propane level analysed to be 96.7%. In addition, it included C2-hydrocarbons 1.25% and C4+heavier hydrocarbons 1.88%. The sulfur level was 5.4 ppm.

In addition to the studies with propane, the role of the lubricating oil on emission formation was studied when utilizing natural gas as a fuel. Two different lubrication oils were utilized. The first oil was Neste 5W-30 Oil (oil 1) and the other Shell Mysella SAE40 Oil (oil 2). The oil 2 was same oil that is utilized in power plant gas engines while the oil 1 was a more proper oil for the test engine (passenger car engine). The oil 1 had a sulfur content of 2000 ppm while the sulfur content of oil 2 was >8000 ppm. Details of oil analysis results can be found in Appendix 2. Both oils were aged for minimum 50 hours of driving before conducting any measurements.

The principal layout of the research facility is presented in Figure 15. With the facility, the exhaust flow properties can be adjusted. The exhaust flow and temperature, which both are relevant parameters for catalyst studies, are independently adjusted. In addition, the exhaust gas composition can be modified by injecting e.g. special hydrocarbon components to result an exhaust gas matrix similar to the one in real application (e.g. power plant gas engine).

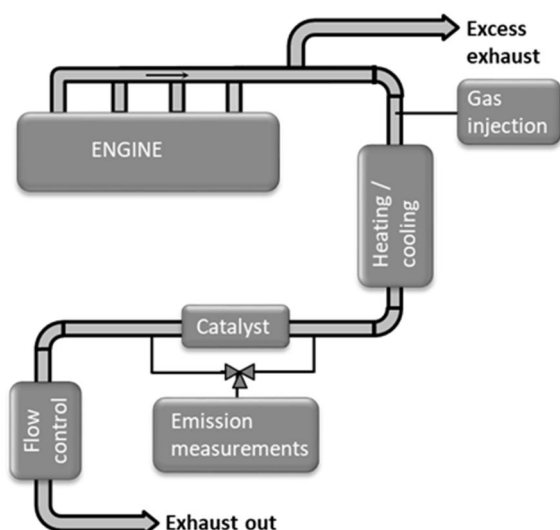


Figure 15 Layout of the research facility.

The catalyst studies were done with propane fuel. Within the scope of this research project, two state of the art catalyst systems were studied similarly. The test set-up for catalyst studies and related emission measurements is presented in Figure 16. The first catalyst system comprised of only one oxidation catalyst element called 'IOXI' while the other system was a combination of selective catalytic reduction (SCR) and a different oxidation catalyst (Oxi). The 'IOXI' was a smaller catalyst ($V = 0,19 \text{ dm}^3$, 40 g/cft Pt) targeting to CO and non-methane hydrocarbon oxidation. The vanadium based SCR had a volume of $5,47 \text{ dm}^3$ and the Oxi placed downstream of the SCR had a volume of $0,72 \text{ dm}^3$ and utilized Pt-catalyst (50 g/cft). In general, the emission measurements were done upstream and downstream of the catalyst system but, in addition, in the case of SCR+Oxi, gaseous compounds were measured with FTIR also between the catalyst elements.

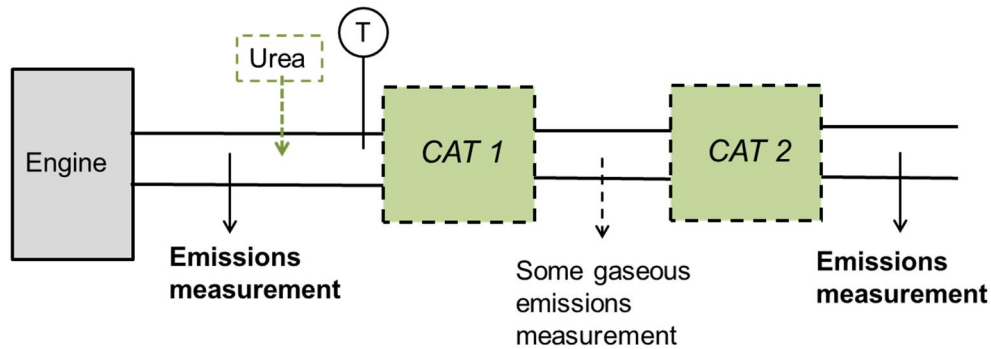


Figure 16 The test set-up for catalyst studies and related emission measurements.

Catalysts were studied with exhaust temperature from 300 to 450 °C (measured upstream of the catalyst) and with exhaust flows of 80 kg/h and 40 kg/h. Prior to actual measurements the catalysts were aged for 50h of driving in mode 1 with exhaust temperature of 400°C and exhaust flow of 80 kg/h.

7.1 Results of lubricating oil studies with NG fuel

The gaseous emissions were not found to change when the lubricating oil was changed. However, the focus in the lubricating oil studies was more on the particle emission formation. With the ISO 8178 method measurements were done at two driving modes, called mode 1 and mode 2, while the EPA 5 + EPA 202 was utilized at mode 1. The PM results, measured with ISO 8178 and EPA 5+EPA 202 methods show no remarkable difference when changing the oil (Fig. 17). The ISO 8178 PM results are slightly higher with oil 2, but when considering the deviation of the PM results, this is minor difference.

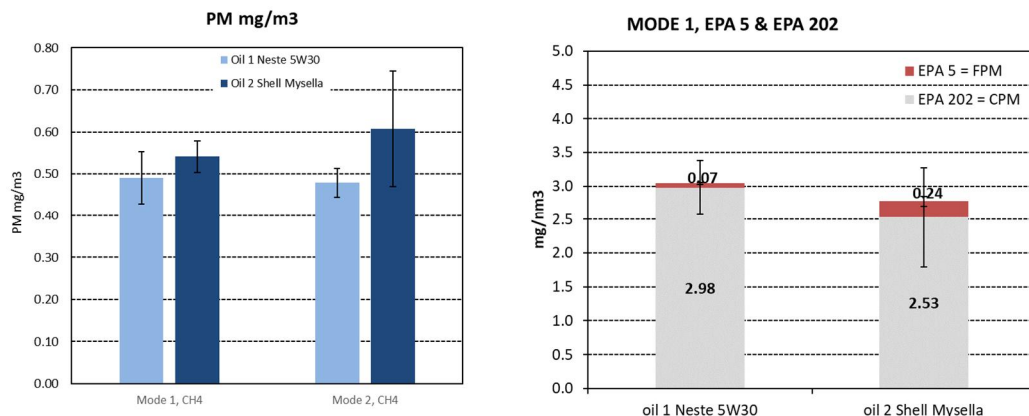


Figure 17 PM measured according to ISO 8178 at two driving modes with both lubricating oils (chart at left hand side) and according to EPA5+EPA 202 method at mode 1 with both lubricating oils.

Elemental analysis were also conducted from the PM filters to find out if traces of lubricating oil are found from the filters. Calcium, which can be regarded as a lubricating oil marker, was found from the filters. With oil 1 slightly higher Ca levels were found from the PM filters and according to the oil composition analysis this oil 1 had higher Ca content, also. However, one should note that the Ca levels found from the PM filters were small and oils are difficult to reliably distinguish based on those. The Ca levels were although measurable and based on those it is explicit that the oil contributes to the PM.

Also in detailed particle studies, differences in exhaust particle number concentrations were relatively small when comparing two used lubricating oils (Figure 18). Size distributions and number concentration measurements showed that, with both oils, the particle size distributions were dominated by very small particles and also nucleation mode was seen. In principle, slightly higher total number concentrations with oil 1 can be related to higher additive content of that oil. Also, slightly larger mean particle size with oil 2 can be caused by higher sulfur content of oil 2. However, it should be noticed that presented number concentrations are mean values of several measurements and lot of variation exist in measured time series.

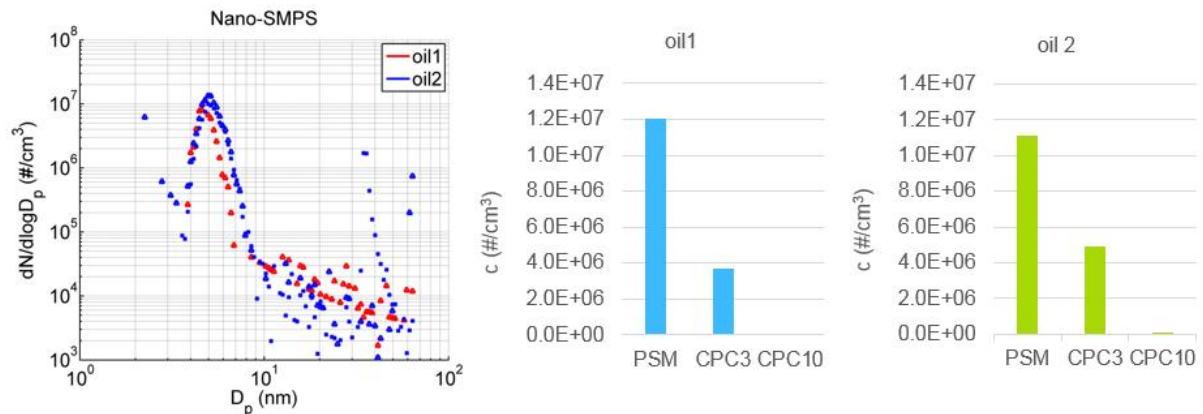


Figure 18 Particle number size distributions and concentrations measured with NG fuel at mode 2 using two different lubricating oils. A particle size magnifier and several condensation particle counters (Airmodus Ltd.) with different cut-points (1.3 nm, 3 nm and 10 nm) were used to measure particle number concentrations.

In terms of secondary particles, lubricating oil has a significant influence on secondary particle emission (Fig. 19). Secondary particle emission was almost three times larger with oil 2 than with oil 1 probably caused by higher sulfur content of oil 2. However, with both lubricating oils, secondary particles consisted mostly of sulfate followed by organic matter.

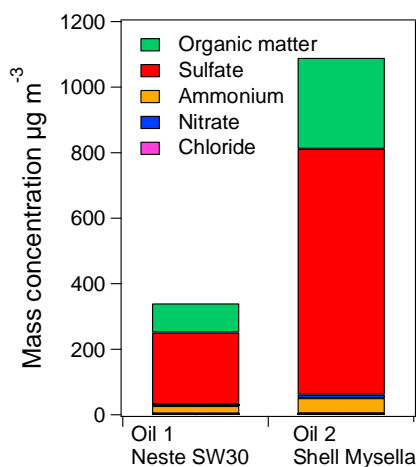


Figure 19 Composition of aged exhaust particulate mass with two lubricating oils.

7.2 Results of propane fuel studies

To compare the emissions produced from propane fuel utilization to natural gas (i.e. methane) utilization the engine mode 1 was run similarly with same torque, speed and power, with both fuels. The results of NO_x (NO & NO_2), CO_2 and CO are shown in Figure 20. With the propane fuel significantly higher NO_x level was measured. This resulted from the increase in NO_2 levels. As expected, the CO_2 was higher with propane compared to methane (i.e. natural gas) use. The CO level was found to be higher with the propane use, also.

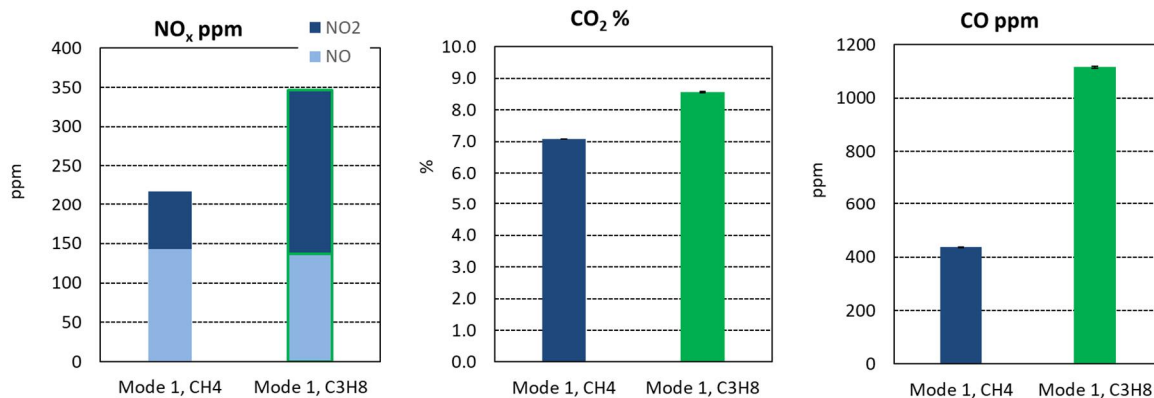


Figure 20 NO_x , CO_2 and CO concentrations from mode 1 run with natural gas (i.e. methane) and with propane as fuel.

The HC composition was expected to be different from propane fuel compared to methane fuel. No methane was found from the exhaust when using propane as fuel. In the case of mode 1, only ethylene and some minor propene were found from the exhaust when propane was used as a fuel (Figure 21). Since the engine manufacturer has seen also propane in the exhaust when running on propane fuel, another driving mode was also tested. This is called mode 2P here. In this mode, in addition to ethylene, propane and propene (and some minor ethane) were found from the exhaust. This mode was then selected for the catalyst studies since the purpose of the catalyst was also to decrease the possible 'propane slip' and with this mode the catalyst's efficiency for propane decrease could be studied.

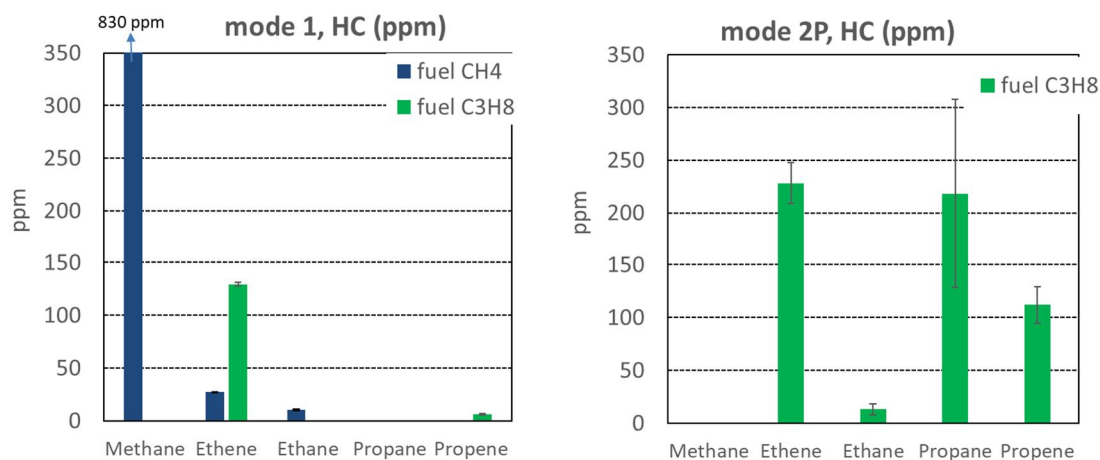


Figure 21 HC composition in the exhaust at mode 1 with methane and propane fuel (chart at left hand side) and at mode 2P with propane fuel. Error bars show the standard deviation.

The HC emissions rates were more variable at mode 2P (with propane fuel) than at mode 1. This can be seen from the high error bars in Figure 21 (chart at right hand side). This was not desirable, but during the measurement campaign, there was not much to do to change this. To have reliable results about the catalyst operation at different conditions (measured at different dates), the engine out emission rates were also measured during each day and the catalyst efficiency was calculated based on that day's engine out emission levels.

The PM (ISO 8178) at mode 1 with propane fuel was $0.57 \pm 0.05 \text{ mg/m}^3$ i.e. on the same level as the one measured with natural gas used as fuel.

Remarkable differences were seen in particle number concentrations between two fuels. For propane, nanoparticle emissions were significantly smaller than for natural gas (Figure 22). With both fuels, the size of exhaust particles was small and sub 10 nm particles strongly dominated the particle number concentration, as seen when the particle number concentrations measured with different devices are compared.

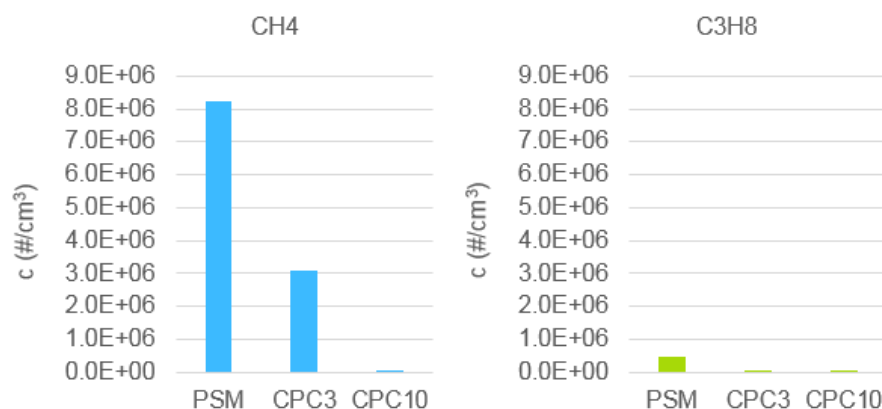


Figure 22 Particle number concentrations measured using NG and propane as a fuel at mode 1 and with oil 2 (Shell Mysella). A particle size magnifier and several condensation particle counters (Airmodus Ltd.) with different cut-points (1.3 nm, 3 nm and 10 nm) were used to measure particle number concentrations.

Regarding the secondary particle emissions with propane fuel, propane seemed to produce lower (~50% lower) secondary particle mass emissions than NG with the same lubricating oil. However, secondary particles from propane contained more nitrate than those from NG in line with increase in NO₂ levels with propane.

7.3 Results of catalyst studies

In general, the efficiency of the smaller oxidation catalyst (IOXI) was found to be lower in terms of any emission component compared to the SCR+Oxi combination. We show here the results for CO conversion, as an example, for both catalyst systems (Figure 23). The CO conversion with the IOXI was 65-70% and approx. 95% with the SCR+Oxi when the exhaust flow was 80 kg/h. By decreasing the exhaust flow to 40 kg/h gave an indication of how a catalyst with a two times higher volume would behave. With the IOXI, the increase in the efficiency was more obvious and from the 65% efficiency with 80 kg/h the efficiency increased to 85% with 40 kg/h. With the SCR+Oxi, having already very high efficiency of 95% with the 80 kg/h the increase was not as clear but still visible reaching clearly above 95%.

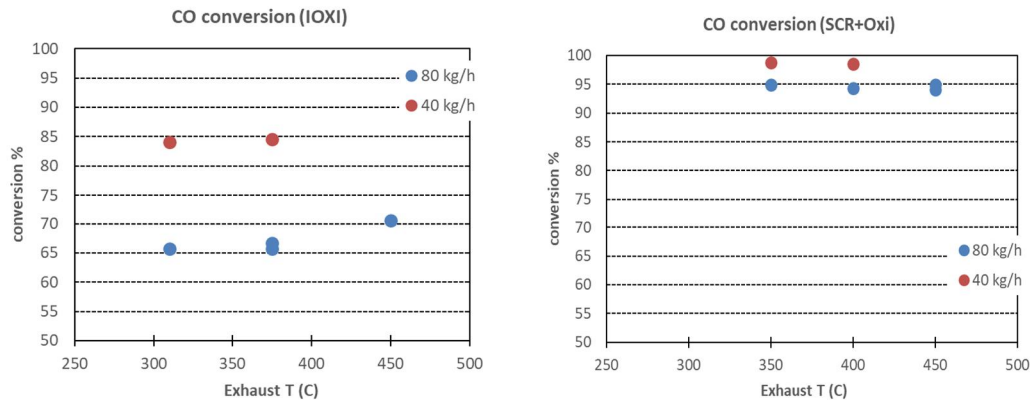


Figure 23 CO conversion for IOXI catalyst (chart at left hand side) and for SCR+Oxi as a function of exhaust temperature at two different exhaust flows.

Similar efficiencies as was seen for CO, was also seen for ethylene, propene and formaldehyde. The propane emission, which was of special interest here, since the fuel was also propane, was only slightly decreased over the IOXI. The highest conversion, recorded at 450 °C, was still below 20%. With the SCR+Oxi some higher conversions for propane were recorded and significant increase in the conversion was found when increasing the exhaust temperature. The highest conversion at 450 °C was approx. 60% (Figure 24).

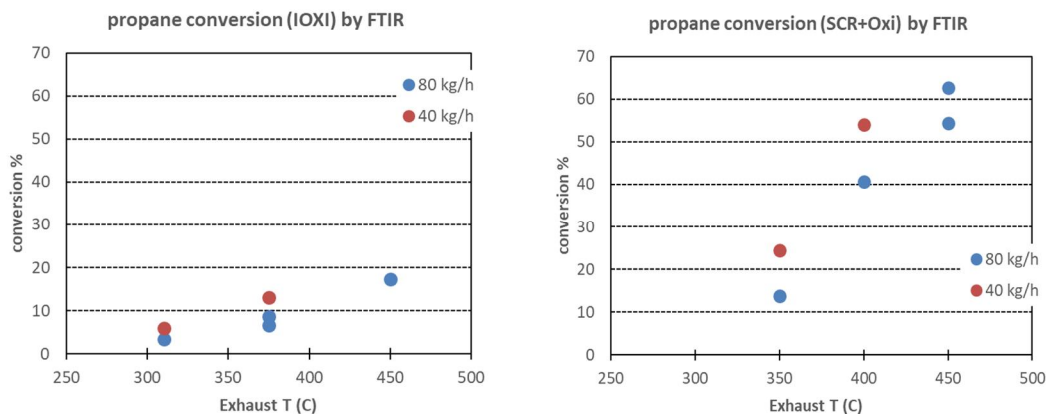


Figure 24 Propane conversion for IOXI catalyst (chart at left hand side) and for SCR+Oxi as a function of exhaust temperature at two different exhaust flows.

Interestingly, the SCR, which targets to NO_x reduction, was found to be effective but not as effective as the same catalyst's operation when utilizing natural gas as a fuel (Fig. 25). There is no clear explanation for this; however, we note that the exhaust compositions are different, especially regarding the hydrocarbon content. With NG, most of the hydrocarbon emissions are methane, which only oxidizes in high temperatures with highly active catalyst, while the SCR has no effect on methane. However, the exhaust from propane combustion, in this case, has, in addition to propane, also propene and ethylene. Moreover, the SCR was found to already oxidize the propene very effectively. No ammonia was measured downstream of the SCR+Oxi combination in any cases.

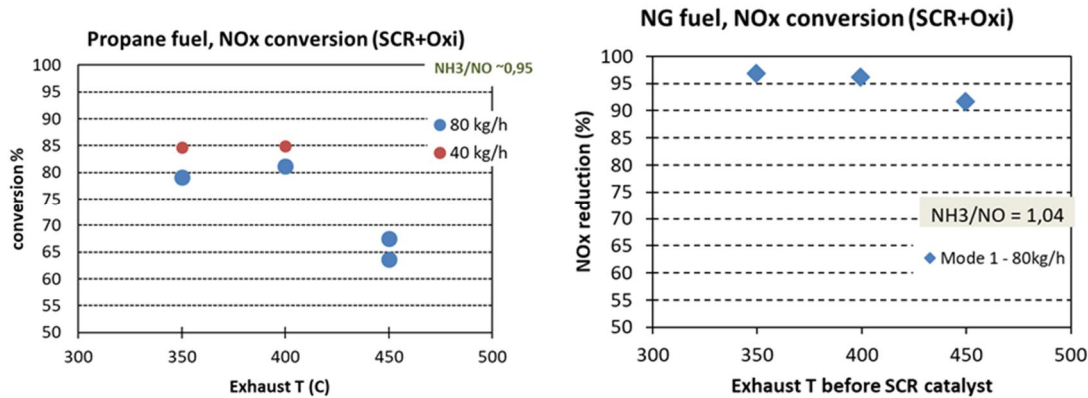


Figure 25 NO_x conversions when utilizing propane as fuel and for comparison when utilizing natural gas as a fuel (CENGE-project results).

PM was measured with ISO 8178 method downstream of both catalysts. The Results are collected to Figure 26. The PM measured downstream of the IOXI at any test conditions was at a similar level than the one measured without any catalyst (i.e. engine out). However, the SCR+Oxi, which was also more effective in oxidizing the CO and hydrocarbons, was also found to decrease the PM. In addition, it seems that the PM level, measured downstream of the SCR+Oxi, depends on the exhaust temperature, with lower temperature lower PM levels were recorded.

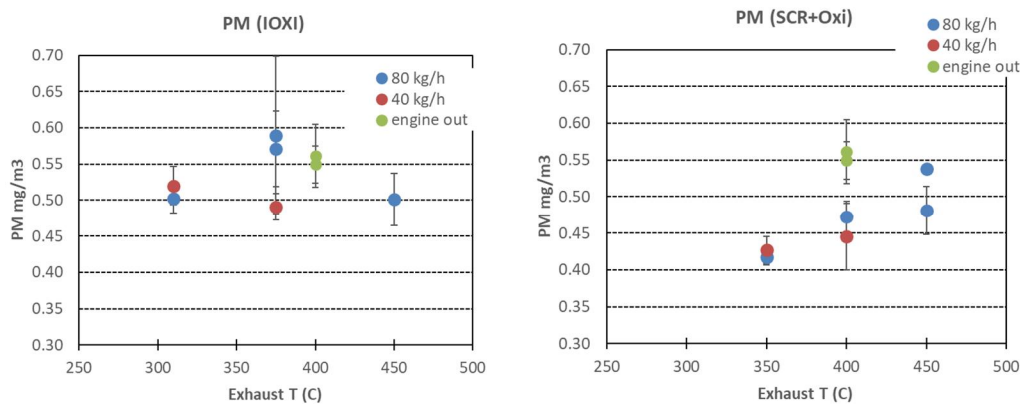


Figure 26 PM measured downstream of the catalysts as a function of exhaust temperature at two different exhaust flows.

Particle number size distribution measurements are presented in Figure 27 with SCR+Oxi combination when the exhaust flow was 80 kg/h. A clear nucleation mode was observed with the highest exhaust temperature (450 °C). In lower exhaust temperature (350 °C) and engine out measurements, particle number concentrations were small in all size ranges.

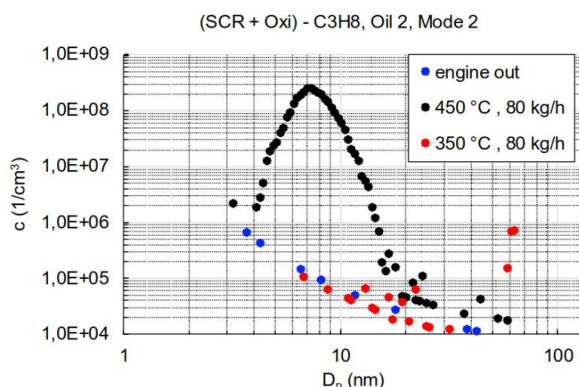


Figure 27 Particle number size distributions measured using SCR+Oxi combination and exhaust flow 80 kg/h with two different exhaust temperatures. Also the engine out situation is presented in the figure.

When the exhaust flow was decreased to 40 kg/h and the exhaust temperature was decreased from 450 °C to 400 °C with SCR+Oxi combination, the size of the exhaust particles and also the particle number concentration decreased.

Secondary particle mass emissions measured downstream of the catalysts were at a similar level or larger than those without any catalyst (i.e. engine out) except for SCR+Oxi at the exhaust flow of 40 kg/h (Fig. 28). Similar to gases and PM, the efficiency of IOXI was found to be lower than that of SCR+Oxi for secondary particle mass emissions. The dependency of secondary particle emission on exhaust temperature was not straightforward as secondary particle mass concentration for IOXI at 375 °C was lower than that at 312 °C. In terms of chemical composition, at each test condition particles were dominated by sulfate whereas the rest of the mass was mostly made of organic matter. For SCR+Oxi at 40 kg/h flow, the mass fraction of sulfate was the largest as the mass fraction of organic matter was as low as 10%. Secondary particles after SCR+Oxi had larger contribution of ammonium (5–10%) than those after IOXI (2–3%). That was probably caused by ammonia from urea used in the SCR in SCR+Oxi.

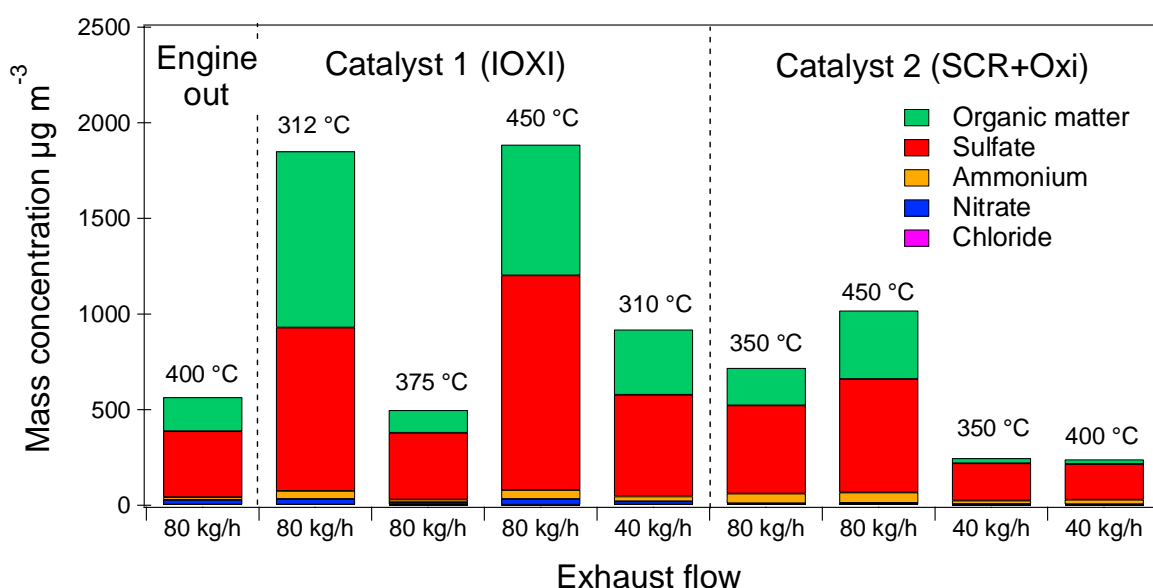


Figure 28 Chemical composition of secondary particles measured upstream (engine out) and downstream of the catalysts at different exhaust temperature and exhaust flow.

8. Workshop

An open workshop presenting the main results of the project was held on 13th November 2018. The agenda of the workshop can be found in the Appendix 3.

9. Conclusions

The main conclusions from NewGas project:

- Large consortium and active joint experiments enabled the utilization of large research infrastructures as well as technical and scientific knowledge, and produced a large collaboration network and largely utilized results.
- The project provided an efficient and interactive platform for instrument testing in gas engine studies
- Understanding of particle emission formation requires detailed measurements and state-of-art aerosol instruments
- Small particles dominate the fresh exhaust aerosol number concentrations in all gas combustion applications studied in this project (laboratory scale gas engine, power plant gas engine and NG burner)
- Nanoparticles were observed mostly semivolatile in measurements conducted in power plant gas engine but non-volatile NG burner measurements. This indicates different formation mechanisms for those particles and highlights the importance of volatility measurements in particle formation studies.
- Gaseous emissions from engine and burner tests differed and, in general, very low emission levels were recorded downstream of the burner.
- The NO_x, CO, methane and formaldehyde concentrations in the biogas engine exhaust were found to be relatively similar to what was measured on the research facility. This indicates that the catalyst studies done at research facility would be relevant also to this real application case utilizing biogas as fuel.
- The lubricating oil was found to contribute to the PM emission.
- Gaseous emissions from natural gas and propane combustion differed remarkably. The PM emissions were although on the same level.
- Changing the fuel from NG to propane was the most significant factor that affect the fresh exhaust aerosol number concentrations in the exhaust of laboratory scale gas engine
- Catalysts were found to have significant effect on the gaseous emissions. In addition, the catalyst with higher activity was found to decrease the PM also.
- Secondary PM emissions from gas engines were much larger than primary PM emissions. Changing the fuel from NG to propane did not change secondary PM emissions while lubricating oil had a large impact on secondary PM. Catalysts were found the influence on the partitioning of chemical species e.g. sulfate in the atmosphere.

10. Publications of the project

Lehtoranta K., Murtonen T., Vesala H., Koponen P., Alanen J., Kuittinen N., Simonen P., Rönkkö T., Saarikoski S., Timonen H., Maunula T., Kallinen K., Korhonen S. Controlling emissions of natural gas engines. Proceedings of the Air and Waste Management Association's Annual Conference and Exhibition, June 5-8, 2017.

Topi Rönkkö; Jenni Alanen; Erkka Saukko; Kati Lehtoranta; Sanna Saarikoski; Panu Karjalainen; Pauli Simonen; Timo Murtonen; Hilikka Timonen; Kimmo Teinilä; Heino Kuuluvainen; Risto Hillamo; Jorma Keskinen. Nanoparticles in natural gas engine exhaust. ETH Conference on Combustion Generated Nanoparticles 2017.

Alanen, J., Karjalainen, P., Teinilä, K., Saarikoski, S., Timonen, H., Keskinen, J. & Rönkkö, T. Role of oxidative exhaust after-treatment in the partition of sulfuric species. European Aerosol Conference 2017.

J. Vanhanen, M. Svedberg, E. Miettinen, J.-P. Salo, and M. Väkevä. Characterization of Dekati Diluter in the 1-20 nm particle size range. International Conference on Nucleation and Atmospheric Aerosols 2017, Helsinki.

J. Vanhanen, M. Svedberg, E. Miettinen, J.-P. Salo, and M. Väkevä. Dekati Diluter characterization in the 1-20 nm particle size range, European Aerosol Conference 2017, Zurich.

M. Svedberg and J. Vanhanen. Fast Size Distribution Measurement for < 10 nm Plasma Generated Particles. ETH conference on combustion generated nanoparticles 2017, Zurich.

J. Vanhanen. Measurement of aerosol particle number concentrations down to 1 nm from car emissions. Internal Combustion Engine (ICE) 2017, Capri.

S. Saarikoski, J. Alanen, H. Vesala, T. Murtonen, M. Isotalo, S. Martikainen, M. Bloss, M. Aurela, T. Maunula, K. Kallinen, J. Torrkulla, H. Timonen, T. Rönkkö and K. Lehtoranta. Characterization of secondary particulate emissions from engine operated by natural gas and propane. NOSA-FAAR (Nordic Society for Aerosol Research - Finnish Association for Aerosol Research) symposium Helsinki 27.-28.3.2018.

S. Saarikoski, J. Alanen, H. Vesala, T. Murtonen, M. Isotalo, S. Martikainen, M. Bloss, M. Aurela, T. Maunula, K. Kallinen, J. Torrkulla, H. Timonen, T. Rönkkö and K. Lehtoranta. Chemical characterization of particles emitted from engine operated by natural gas and propane. International Aerosol Conference, Saint Louis, Missouri, US 2.-7.9.2018

M. Isotalo, J. Alanen, J. Vanhanen, S. Martikainen, H. Vesala, R. Pettinen, S. Saarikoski, M. Aurela, P. Simonen, M. Kettunen, M. Väkevä, H. Timonen, K. Lehtoranta, J. Keskinen and T. Rönkkö. Nanoparticle emissions from a gas engine – effects of gas and lubricant oil composition. International Aerosol Conference, Saint Louis, Missouri, US 2.-7.9.2018

Joonas Vanhanen, Jenni Alanen, Kati Lehtoranta, Sanna Saarikoski, Minna Väkevä, Topi Rönkkö. Sizing Sub-10 nm Particles from Engine Emissions. International Aerosol Conference, Saint Louis, Missouri, US 2.-7.9.2018

J. Alanen, N. Kuittinen, R. Hietikko, H. Vesala, S. Saarikoski, K. Lehtoranta, J. Keskinen and T. Rönkkö. Nanoparticle study on a catalytic natural gas burner. Aerosol Technology, AT2018, June 18-20, 2018 Bilbao, Spain.

Lehtoranta K., Vesala H., Pettinen R., Murtonen T., Isotalo M., Alanen J., Rönkkö T., Saarikoski S., Timonen H. Particle emissions from gas engine utilizing natural gas and

propane as fuel. 22nd ETH-Conference on Combustion Generated Nanoparticles, June 18th - 21st, 2018 at ETH Zurich, Switzerland.

Mia Isotalo, Fanni Mylläri, Sanna Saarikoski, Hannu Vesala, Teemu Lepistö, Kati Lehtoranta and Topi Rönkkö. Nanoparticle emissions from a biogas engine. *An abstract submitted to European Aerosol Conference 2019, August 25-30, Göteborg, Sweden.*

Kati Lehtoranta, Hannu Vesala, Timo Murtonen, Jenni Alanen, Mia Isotalo, Sampsa Martikainen, Topi Rönkkö, Sanna Saarikoski. Reduction of natural gas engine emissions using catalysts. A paper and presentation at 11. DESSAU GAS ENGINE CONFERENCE April 11-12, 2019.

11. References of literature outside project

Alanen, J., Saukko, E., Lehtoranta, K., Murtonen, T., Timonen, H., Hillamo, R., Karjalainen, P., Kuuluvainen, H., Harra, J., Keskinen, J., Rönkkö, T. The formation and physical properties of the particle emissions from a natural gas engine. *Fuel* 162, 155–161, 2015.

IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp, doi:10.1017/CBO9781107415324.

Kajolinna, T., Aakko-Saksa, P., Roine, J., Kåll, L. Efficiency testing of three biogas siloxane removal systems in the presence of D5, D6, limonene and toluene. *Fuel processing technology* 139, 242-247, 2015.

Lehtoranta, K., Murtonen, T., Vesala, H., Alanen, J., Rönkkö, T., Timonen, H., Saarikoski, S., Maunula, T., Kallinen, K., Korhonen, S. Natural gas engine emission reduction by catalysts. Manuscript in preparation, 2016.

Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., and Pozzer, A.: The contribution of outdoor air pollution sources to premature mortality on a global scale, *Nature*, 525, 367-371, 2015.

Murtonen, T.; Lehtoranta, K.; Korhonen, S.; Vesala, H. Imitating emission matrix of a large natural gas engine opens new possibilities for catalyst studies in engine laboratory. In: CIMAC congress, June 6-10, 2016.

Appendixes

Appendix 1 - EPA 5 + EPA 202 description (in Finnish)

Appendix 2 - lubrication oil analysis results

Appendix 3 - workshop agenda

Appendix 4 – measurement setup for detailed particle studies in Viikinmäki measurement campaign

1. EPA5 & 202 näytteenotto

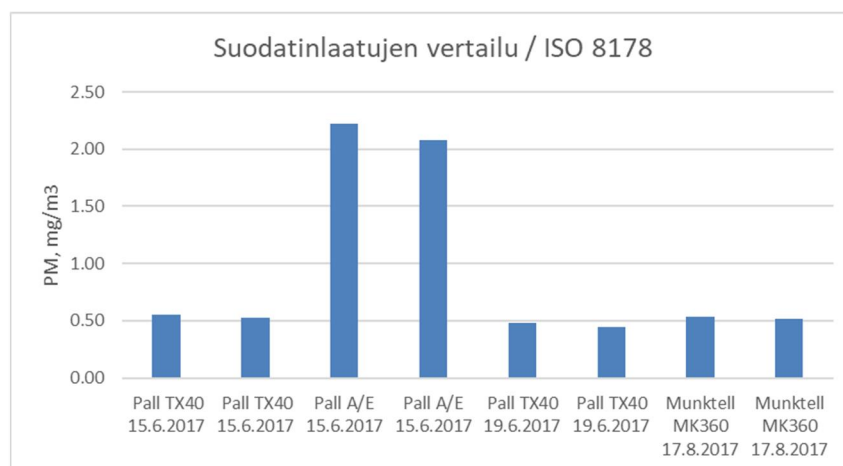
1.1. Käytetyt laitteet ja tarvikkeet

- Lasisondi (150 cm, sisähalkaisija 6 mm, kärjen halkaisija)
- Teräksinen sondin suojaputki, jossa ulkokehällä vaippa lämmitysilmaa varten
- Paineilmalämmitin säätimellä (sondin lämmitys)
- Kuumailmapuhallin (EPA 5 suodatinpidikkeen lämmitys)
- 2 x Lasinen suodatin pidike
- Peltisuoja EPA 5 suodatinpidikkeelle
- EPA 5 suodatin Munktell MK360 (kvartsi), 47 mm
- EPA 202 suodatin Pall Zefluor 1 µm, 47 mm
- Lasinen jäähdytin
- Impinger-pullo lyhennetyllä insertillä
- 3 x Impinger-pullo normaalilla insertillä
- 2 x Jäähdytinvessiallas
- Näytteenottoyksikkö, jossa pumppu ja kaasukello

1.1.1. EPA5 suodatinmateriaalit

VTT:llä tehdyissä esikokeissa havaittiin, että EPA5 menetelmän suosittlemalle suodatinlaadulle (Glass fiber filter, without organic binder, Pall A/E) kertyi odotettua merkittävästi enemmän hiukkasmassaa. Tämän perusteella tehtiin ISO 8178 menetelmällä suodatinlaatuja vertailumittauksia. EPA 5 menetelmää ei käytetty suodatinvertailussa sen hitauden ja työläyden vuoksi.

Vertailumittauksissa havaittiin, että Pall A/E suodatinlaadulla suodattimelle kertynyt massa oli nelinkertainen verrattuna ISO 8178 menetelmässä käytettävään Pall TX40 suodatinlaatuun. Sen sijaan Munktell MK360 suodattimella saatiin lähes sama tulos, kuin Pall TX40 suodatinlaadulla, eroa tulosten välillä oli n. 20%. (Kuva 1)



Kuva 1, Suodatinlaatuja vertailun tulokset.

Suodatinvertailujen perusteella voitiin päätellä, että Pall A/E suodatin reagoi jonkin pakokaasussa olevan yhdisteen (mahdollisesti rikkiyhdisteet) kanssa ja suodattimelle muodostuu artefaktaksi luokiteltavaa massaa. Tästä syystä suodatinlaatu varsinaisia mittauksia varten vaihdettiin kvartsisuodattimiksi (Munktell MK360). Tämä on myös sallittua EPA5 menetelmän ohjeistuksen mukaan (In sources containing SO₂ or SO₃, the filter material must be of a type that is unreactive to SO₂ or SO₃).

1.2. Mittauksen valmistelu

Mittauksissa käytettävät EPA 5 näytesuodattimet esikäsitellään 700 asteisessa uunissa tunnin ajan. Tämän jälkeen suodattimien annetaan stabiloitua punnitushuoneessa vakio-olosuhteissa useampi vuorokausi, siten että suodattimen massa on stabiloitunut. Ennen mittausta EPA5 näytesuodattimet punnitaan ja asetetaan puhtaaseen suodatinpidikkeeseen. EPA202 suodattimet eivät vaadi esikäsitelyä ja niitä ei tarvitse punnita mittausta varten. EPA202 suodattimelta ei määritetä massaa punnitsemalla, vaan se uutetaan mittauksen jälkeen ja massa määritetään uutteen haihdutusjäännöksestä.

Ennen mittauksen aloittamista lasisondi ja EPA5 suodatinpidike lämmitetään tarvittavaan lämpötilaan. Sondi työnnetään teräksisen suojaputken sisälle ja suojaputken ulkovaippaan johdetaan lämmitettyä paineilmaa. Tarvittavan lämmityksen asetukset on määritettävä tapauskohtaisesti. Suodatinpidike asetetaan suojapellin sisälle ja siihen puhalletaan lämmintä ilmaa kuumailmapuhaltimella. Kuumailmapuhaltimen lämpötila-asetus ja puhallusnopeus haetaan kokeilemalla sopiviksi. Sondin ja suodatinpidikkeen annetaan lämmitä vähintään 15 min ennen mittauksen aloittamista. Suodatinpidikkeen lämpötilaa seurataan koepenkin tiedonkeruusta ja tavoitelämpötila on 100 – 110 °C.

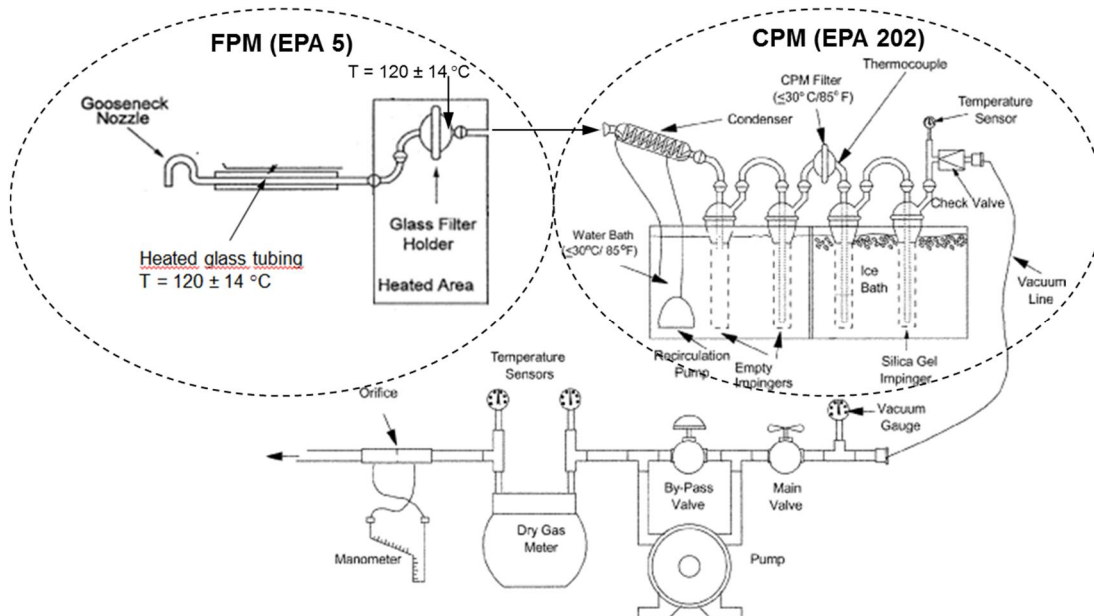
Sondin ja suodatinpidikkeen lämmityksen lisäksi jäähdytysaltaat laitetaan vähintään tuntia ennen mittauksen aloittamista päälle, jotta niiden lämpötilat ehtivät tasoittua. Ensimmäinen jäähdytysallas asetetaan 25 asteen lämpötilaan ja toinen 0 asteen lämpötilaan. Ensimmäisessä jäähdytysaltaassa on kiertopumppu, jonka avulla nestettä kierrätetään jäähdyttimessä. Jäähdyttimen nestekierto on hyvä kytkeä päälle samalla kun suodatinpidikettä aletaan lämmittää. Ensimmäiseen altaaseen sijoitetaan EPA 202 menetelmään kuuluvat impinger-pullot (normaali ja lyhennetyllä insertillä). Ensimmäisen jäähdytysaltaan tarkoituksena on stabiloida näytekaasun lämpötila ennen EPA 202 suodatinta. Samalla jäähdyttimeen ja impinger-pulloihin voi kondensoitua orgaanisia yhdisteitä.

Jälkimmäinen jäähdytysallas on EPA202 suodattimen jälkeen ja siihen sijoitetaan kaksi normaalia impinger-pulloa, joista ensimmäiseen tulee vettä n. 100 ml ja jälkimmäiseen 200-250 g silikageeliä. Pullojen tarkoituksena on kuivata näytekaasu kaasukelloa varten. Pulloihin kertyneen veden määrää ei määritetä, koska näytekaasun kosteus saadaan FTIR-mittauksesta.

1.3. Mittaus

Kun sondi ja suodatinpidike ovat lämmenneet sekä jäähdytysaltaiden lämpötilat stabiloituneet, työnnetään sondi pakoputkeen ja liitetään sondi suodatinpidikkeeseen ja suodatinpidike muuhun näytelinjastoon (lasinen jäähdytin, impinger-pullot, EPA202 –suodatinpidike ja näytteenottoyksikkö, kuva 2). Ennen näytteenoton aloittamista kirjataan kaasukellon lukema

talteen. Näytteenotto aloitetaan avaamalla näytteenottoyksikön venttiili ja sen jälkeen käynnistetään näytepumppu. Näytteenoton aloittamisen jälkeen seurataan EPA5 suodatinpidikkeen lämpötilaa ja sen saavuttaessa arvon $120\text{ }^{\circ}\text{C}$, voidaan suodatinpidikettä lämmittävä kuuma ilmapuhallin sammuttaa. Mittauksen aikana valvotaan suodatinpidikkeen lämpötilaa ja tarvittaessa muutetaan sondin lämmityksen parametreja.



Kuva 2, EPA5 ja 202 näytelinjasto.

Mittauksen aikana tallennetaan EPA5 ja 202 suodatinpidikkeiden lämpötila, sekä kaasukellon sisäänmenon ja ulostulon lämpötilat. Näytelinjaston tiiveys tarkastetaan mittauksen aikana johtamalla näytteenottoyksikön kaasukelloilta tuleva näytekaasu Horiba PG-250 analysaattorille. Analysaattorilla mitataan normaalisti pakokaasun CO, CO₂, NO_x, ja O₂ -pitoisuuksia. Mitattaessa kaasukelloilta tulevaa näytekaasua ei CO₂/CO pitoisuus saa muuttua enempää kuin 4 % verrattuna pakokaasun pitoisuuteen.

Mittaus lopetetaan sammuttamalla ensin näytepumppu ja sitten suljetaan näytteenottoyksikön venttiili. Lisäksi kaasukellon lukema kirjataan talteen.

1.4. Näytteiden käsittely

Mittauksen päätyttyä sondi otetaan pois pakoputkesta ja sondin annetaan jäähtyä vähintään 30 min ennen kuin se siirretään puhdashuoneeseen huuhtelua varten. Myös EPA5 suodatinpidikkeen annetaan jäähtyä ennen näytesuodattimen pois ottamista. EPA5 näytesuodatin asetetaan petrimaljaan ja viedään punnitushuoneeseen stabiloitumaan punnitusta varten. Suodatinpidikkeet ja näytelinja huuhdellaan/pestään myöhemmin tässä kuvauksessa kerrotulla tavalla.

Kun sondi ja suodatinpidike on saatu jäähtymään, aloitetaan EPA202 linjaston typpihuuhtelu. Huuhtelu kestää tunnin ja siinä käytetään 5.0 laadun typpeä. Typen virtaus asetetaan arvoon 13 l/min. Ennen typpihuuhtelua näytelinjastosta irrotetaan lasinen jäähdytin ja ensimmäinen impinger-pullo (lyhyt insertti). Molempiin kondensoitunut vesi kaadetaan jälkimmäiseen impinger-pulloon ja varmistetaan, että pullon insertin pää yltää veden pinnan alapuolelle. Mikäli

näin ei ole, lisätään pulloon milli-Q-vettä siten, että insertin pää on noin 1 cm veden pinnan alapuolella. Tämän jälkeen kytketään typpilinja impenger-pullon sisäänmenoon ja aloitetaan typpihuuhtelu. Huuhtelun tarkoituksena on poistaa mahdollisia rikkiyhdisteitä näytelinjastosta. Typpihuuhtelun jälkeen EPA 202 suodatin ja näytelinjasto toimitetaan uutettavaksi ja pestäväksi epäorgaanisten ja orgaanisten yhdisteiden määrittämistä varten.

2. CPM:n analysoiminen VTT:llä

2.1. Käytetyt aineet ja tarvikkeet

- n-Heksaani LiChrosolv® (Merck 1.04391.2500)
- Asetoni , ULTRA RESI-ANALYZED™, ACS Reagent, For Organic Residue Analysis (BAKR9254.2500)
- Milli-Q-vesi (VTT)
- Silikageeliä
- Erotussuppiloita ,1 l
- Alumiinisia numeroituja punnitusmaljoja, 30 ml
- Ruskeita näytepulloja, 500ml
- Dekanterilaseja 250 ja 400 ml
- Mittalaseja 50, 100 ja 250 ml
- Pesupullo heksaanille, 500 ml Teflonia
- Pesupullo asetonille , 500 ml HDPE-laatua
- Pesupullo milli-Q-vedelle, 500 ml HDPE-laatua
- CPM-suodatin, Zeflour,Pall 1.0 um, 47 mm, 100 % Teflon
- Statiivi renkaalla

2.2. Käytetyt laitteet

- Vaaka, Sartorius SE2-F, resoluutio 0,001 mg
- Ultraäänihaude, VWR ultrasonic bath, USC500T
- Eksikaattori, jossa kuivausaineena oranssi silikageeli, partikkelikoko 2-5 mm

2.3. Analyysin alkuvalmistelut

Näytteiden käsittelyä ja analysointia varten tilattiin kahden vetokaapin pesu.

Kaikki analyyseissä ja näytteenotossa käytetyt lasitavarat pestiin ennen käyttöä seuraavalla tavalla:

- Vesipesu joko koneessa tai käsin. Konepesuohjelma sisälsi kaksi milli-Q-vesi huuhtelua, jonka lisäksi lasitavara huuhdeltiin vielä kaksi kertaa käsin milli-Q-vedellä. Tiskikone oli yleisessä käytössä ja siellä voitiin pestä hyvinkin likaisia astioita, siksi vielä kaksi lisähuuhtelua käsin.
- kolme kertaa pesu asetonilla.
- kolme kertaa pesu heksaanilla.

Pestyt astiat säilytettiin suljetuissa muovilaatikoissa kontaminaatioiden välttämiseksi.

Punnitusmaljoina käytettiin alumiinisia 30 ml haihdutusmaljoja, joita jouduttiin madaltamaan muutama milli, jotta ne mahtuivat Sartoriuksen SE2-F vaakaan. Maljoihin merkittiin tunnisteeksi juokseva numerointi. Maljat pestiin käsin vedellä, huuhdeltiin tislattulla vedellä ja lopuksi asetonilla ja annettiin kuivua vetokaapissa. Puhtaita maljoja säilytettiin eksikaattorissa ja niitä käsiteltiin ainoastaan pinseteillä.

Ennen näytteiden analysoimista käytetystä vedestä, asetonista ja heksaanista tehtiin haihdutusjäännös (nollanäyte) mittaamalla puhtaaseen 250 ml:n dekantterilasiin orgaanista liuoksia 150 ml. Orgaaniset liuokset haihdutettiin vetokaapissa huoneenlämmössä noin 10 ml:iin, jonka jälkeen ne siirrettiin puhtaaseen punnittuun alumiiniseen 30 ml haihdutusmaljaan. Maljat annettiin haihtua kuiviin vetokaapissa huoneenlämmössä. Veden haihdutusjäännös tehtiin mittaamalla 150 ml milli-Q-vettä puhtaaseen 250 ml dekantterilasiin ja haihduttamalla se lämpölevyllä noin 10 ml, joka jälkeen se siirrettiin puhtaaseen punnittuun alumiiniseen 30 ml haihdutusmaljaan. Maljan annettiin haihtua kuiviin vetokaapissa huoneenlämmössä. Haihtuneet maljat siirrettiin eksikaattoriin, jossa kuivaus aineena käytettiin silicageeliä. Maljoja pidettiin 24 h eksikaattorissa ennen ensimmäistä punnitusta, jonka jälkeen niitä punnittiin vähintään 6 tunnin välein, kunnes saavutettiin vakiopaino eli peräkkäisten punnitusten välinen ero oli pienempi kuin 0,1 mg. Punnituksissa käytettiin Sartoriuksen SE2-F vakaa, jonka resoluutio oli 0,001 mg. EPA202 vaatimus haihdutusjäännökselle oli <0,1 mg/100 g, jonka käytetyt reagenssit täyttivät. Reagenssien haihdutusjäännökset on esitetty Taulukossa 1.

Taulukko 1, Nesteiden nollanäyttekokeiden tulokset.

	Haihdutusjäännös, mg/100g
Heksaani	0.009
Asetoni	0.053
milli-Q-vesi 1	0.019
milli-Q-vesi 2	0.033

Lisäksi tehtiin kahdelle CPM-suodattimelle (Zeflour) ultraääninuutto ensin 3x10 ml:llä milli-Q-vettä ja sitten 3x10 ml:llä heksaania suodattimen aiheuttaman CPM massan lisääntymisen selvittämiseksi. Uutteet haihdutettiin EPA202 menetelmän mukaisesti. EPA202 vaatimus suodattimen aiheuttamalle CPM:lle on < 0,5 mg. VTT:n kokeiden tulokset on esitetty Taulukossa 2

Taulukko 2, CPM-suodattimien uuttokokeet.

Uutettu suodatin	m_i , mg	m_o , mg	CPM, mg
Zefluor 1	0.067	0.014	0.081
Zefluor 2	0.047	0.014	0.061

2.4. EPA 202 ja EPA 5 näytteen käsittely

2.4.1. EPA 5

Näytesondi irrotettiin näytteenoton jälkeen ja siirrettiin jäähtymään puhdistilahuoneeseen. Sondi huuhdeltiin 3 x asetonilla 500 ml näytepulloon, johon oli merkitty näytetiedot. EPA5 suodatin poistettiin pidikkeestä ja vietiin petrimaljassa temperoitumaan vakio-olosuhdehuoneeseen. EPA5 pidikkeen etuosa, ennen suodatinta, huuhdottiin asetonilla samaan näytepulloon kuin sondi.

Arvioitiin asetonin tilavuus (yleensä n. 40-50 ml) ja siirrettiin 250 ml dekantterilasiin haihtumaan vetokaappiin. Annettiin haihtua huoneenlämmössä n. 10 ml, jonka jälkeen asetoni siirrettiin vakiopainoon punnittuun alumiiniseen punnitusmaljaan, jossa näyte haihdutettiin kuiviin. Kuiva haihdutusmalja siirrettiin eksikaattoriin, jossa sitä pidettiin vähintään 24 h ennen ensimmäistä punnitusta, jonka jälkeen haihdutusmaljaa punnittiin vähintään 6 h välein kunnes saavutettiin vakiopaino.

2.4.2. EPA 202

2.4.2.1. Näytelinjaston huuhtelu

Näytelinjasto siirrettiin moottorikoetilasta 1 h typpihuuhtelun jälkeen laboratorioon, jossa CPM-suodatin irrotettiin pidikkeestään ja siirrettiin puhtailla pinseteillä Petrimaljaan.

Ensimmäiseen impingeriin kondensoitunut vesi siirrettiin ruskeaan näytepulloon, johon oli merkitty näytetiedot esim. EPA_202_01 merkintä "Vesifaasi". Missään testeissä toiseen impingeriin ei kondensoitunut vettä. Kondensoituneen veden määrä arvioitiin ja merkittiin se näytetaulukkoon. Kondensoituneen veden määrä vaihteli mode 1 testeissä 62-67 ml välillä ja mode 4 testeissä 53-62 ml välillä paitsi testissä EPA202-13 (mode 4), jossa ei käytetty typpihuuhtelua, kondensoituneen veden määrä oli 86 ml. Näytetaulukko liitteenä 1.

Kaikki CPM näytelinjan osat eli EPA5 suodatinpidikkeen takaosa termoelementeineen, kondensaattori, kumpikin impinger ja näiden liitososat sekä CPM-suodatinpidikkeen etuosa huuhdeltiin ensin kaksi kertaa n. 25 ml milli-Q-vettä. Nämä huuhteet lisättiin näytepulloon, jossa oli merkintä "Vesifaasi".

Vesihuuhtelun jälkeen CPM näytelinjaston osat huuhdeltiin ruskeaan näytepulloon ensin kerran asetonilla ja sen jälkeen vielä kaksi kertaa heksaanilla. Nämä huuhteet lisättiin samaan näytepulloon, jossa oli merkintä "Orgaaninen faasi".

Näytelinjaston huuhteluun käytetyn veden ja orgaanisen liuottimen määrä arvioitiin ja merkittiin näytetaulukkoon.

2.4.2.2. CPM –suodattimen uutto

Epäorgaaninen veteen liukeneva osuus uutettiin CPM-suodattimesta taittelemalla se pinsettien avulla neljään osaan ja laittamalla se 50 ml mittalasiin. Mittalasiin lisättiin vettä niin, että suodatin peittyi, kuitenkin vähintään 10 ml. Mittalasi laitettiin ultraäänihauuteeseen ja suodatinta

uutettiin vähintään 2 min. Uuton jälkeen vesi yhdistettiin näytepulloon, jossa oli merkintä "Vesifaasi". Uutto vedellä toistettiin vielä kaksi kertaa.

Orgaaninen liukeneva CPM uutettiin suodattimesta lisäämällä vesiuuton jälkeen mittalasiin hekkaania niin, että suodatin peittyi, kuitenkin vähintään 10 ml. Suodatinta uutettiin ultraäänihauteessa vähintään 2 min. Uuton jälkeen hekkaani yhdistettiin näytepulloon, jossa oli merkintä "Orgaaninen faasi". Suodattimen uutto hekkaanilla toistettiin vielä kaksi kertaa.

Testeissä EPA202_02 – 09 CPM-suodattimien annettiin temperoitua yön yli vakio-olosuhdehuoneessa ennen punnitsemista, jonka jälkeen ne vasta uutettiin. Testien EPA202_10 – 14 CPM-suodattimet uutettiin heti kokeen jälkeen ja vietiin vasta sen jälkeen vakio-olosuhdehuoneeseen temperoitumaan ja punnittavaksi. EPA202 menetelmässä ei punnita CPM-suodattimia. Punnitusten avulla haluttiin nähdä, kuinka paljon suodattimelle kertyy massaa.

2.4.2.3. Yhdistetyn vesifaasin uutto hekkaanilla

Yhdistetty vesifaasi, joka siis sisälsi näytteenoton aikana kondensoituneen veden, näytelinjaston huuhtelu veden ja CPM-suodattimen uuttoveden, kaadettiin 1 l erotussuppiloon.

Erotussuppiloon lisättiin n. 30 ml hekkaania. Erotussuppiloon sekoitettiin hyvin ja annettiin faasien erottua. Alempi vesifaasi laskettiin erotussuppilosta takaisin alkuperäiseen näytepulloon ("Vesifaasi") ja ylempi orgaaninen faasi (hekkaani) otettiin mittalasiin talteen. Faasien erottamisessa kiinnitettiin erityistä huomioita siihen, ettei vettä joutunut orgaaniseen faasiin. Vesifaasi kaadettiin takaisin erotussuppiloon ja uutto n. 30 ml hekkaania toistettiin vielä kahdesti. Vesifaasin uutosta talteen kerätyn orgaanisen faasin määrä vaihteli 84 -87 ml. Talteen otettu uutosto yhdistettiin näytepulloon, jossa oli merkintä "Orgaaninen faasi".

2.4.2.4. Faasien haihduttaminen

Vesifaasi

Vesifaasi kaadettiin näytepullosta puhtaaseen 400 ml dekantterilasiin ja siirrettiin haihtumaan lämpölevylle. Kun näytettä oli jäljellä n. 50-40 ml lämpölevyn säätöä pienennettiin ja loppuhaihdutus reiluun 10 ml tehtiin miedolla lämmöllä. Tämän jälkeen näyte siirrettiin punnittuun puhtaaseen alumiiniseen punnitusmaljaan ja annettiin haihtua kuiviin vetokaapissa huoneenlämmössä. Haihdutuksen jälkeen punnitusmaljan kuivaamista jatkettiin eksikaattorissa, jossa kuivausaineena käytettiin silicageeliä. Haihdutusmaljaa pidettiin eksikaattorissa vähintään 24 h ennen ensimmäistä punnitusta, jonka jälkeen punnitusta jatkettiin vähintään 6 h välein, kunnes saavutettiin vakiopaino eli peräkkäisten punnitusten välinen ero oli pienempi kuin 0,100 mg. Punnitustuloksena saatiin m_i eli epäorgaaninen CPM massa 0,001 mg tarkkuudella.

Orgaaninen faasi

Orgaaninen faasi eli näyte, joka muodostui näytelinjaston osien huuhtelusta asetonilla ja 2xhekkaanilla, CPM-suodattimen ja vesifaasin hekkaaniuutosta, siirrettiin puhtaaseen 400 ml dekantterilasiin, jossa se annettiin haihtua reiluun 10 ml. Tämän jälkeen näyte siirrettiin punnittuun puhtaaseen alumiiniseen punnitusmaljaan ja annettiin haihtua kuiviin vetokaapissa

huoneenlämmössä. Vetokaappihaihdutuksen jälkeen punnitusmaljan kuivaamista jatkettiin eksikaattorissa ja punnittiin vakiopainoon kuten epäorgaaninen faasi. Punnitustuloksena saatiin m_o eli orgaaninen CPM massa 0,001 mg tarkuudella.

2.4.2.5. CPM laskenta

Kokonais CPM-massa laskettiin:

$$m_{cpm} = m_i + m_o - m_{fb},$$

Jossa,

m_i = epäorgaaninen CPM massa, mg

m_o = orgaaninen CPM massa, mg

m_{fb} = kokonais CPM-massa kenttänollasta (FTRB), mg

Lopullinen CPM konsentraatio laskettiin mg/m^3

$$C_{cpm} = m_{cpm} / V_m$$

Jossa ,

V_m = kuivan kaasunäytteen tilavuus NTP:ssä (20 °C, 1013.25 mbar)

2.4.2.6. Yleistä

Meillä oli käytössä ns. dust pan eli tyhjä punnittu alumiininen haihdutusmalja, joka pidettiin samaan aikaan vetokaapissa, kun varsinaisia näytteitä haihdutettiin kuiviin. Tällä seurattiin ympäristöstä tulevan artefaktin määrää. Taulukossa 3 on joitakin esimerkkejä tyhjän haihdutusmaljan painonmuutoksista testien aikana.

Taulukko 3, Alumiinisen haihdutusmaljan painonmuutos.

pvm	Dust pan, Painonmuutos, mg
8.6.2017	0.007
9.6.2017	0.006
15.6.2017	0.008
19.6.2017	0.002
20.6.2017	0.002
22.6.2017	0.000

Orgaaniset haihdutusjäännökset sekä mode 1:ssä, että mode 4:ssä olivat vakiopainossa heti toisen punnituksen jälkeen. Epäorgaaniset haihdutusjäännökset mode 4:ssä saavutti vakiopainon kolmannen punnituksen jälkeen, mutta mode 1:ssä vakiopaino saavutettiin 3 - 6 punnituskerran jälkeen. Kaikissa epäorgaanisissa haihdutusjäännösmassoissa tapahtui vielä tämänkin jälkeen massavähennemää, mutta se oli kuitenkin pienempää kuin 0,100 mg/vrk. Näytteiden massahäviämä tuli korostetusti esiin, kun käytössä oli 0,001 mg tarkkuusluokan vaaka. EPA202 menetelmän tarkkuusvaatimus vaa'alle on 0,1 mg. EPA Method 202 Best Practices Handbook suosittelee vaa'an tarkkuudeksi 0,01 mg mitattaessa pieniä CPM massoja.

Epäorgaanisten massojen katsottiin siis näissä kokeissa saavuttaneen vakiopainon, eikä niille tehty NH₄OH-titrausta happojen neutralisoimiseksi.

Vaa'an stabiilisuutta seurattiin punnitsemalla aina 200 mg E2 tarkkuusluokan punnus ennen haihdutusmaljojen punnittusta.

Lasitavaraa ei pesujen jälkeen uunitettu 300 °C:ssa 6 h, koska sondi ei olisi mahtunut uuniin. Uunituksen vaihtoehtona EPA202 menetelmässä on kenttänollan tekeminen ennen testien aloittamista näytelinjaston puhtauden varmistamiseksi. Kenttänollassa huuhdellaan kaikki näytelinjaston osat ensin kaksi kertaa vedellä (epäorgaanisen osa) ja sen jälkeen kerran asetonilla ja kaksi kertaa heksaanilla (orgaaninen osa). Nämä haihdutetaan kuiviin kuten näytteen. Kenttänollaa ei tehty. Lasitavarat olivat käyttämättömiä ja FTRB oli <2 mg (kts.2.4.2.7.).

2.4.2.7. Nollakokeet

EPA 202 menetelmässä on kuvattu kaksi erilaista kentällä tehtävää "nollakoetta". "Field train proof blank" (kenttänolla) ohjeistetaan tehtäväksi silloin kun lasitavaroita ei ole uunitettu pesun jälkeen (kts. 2.4.2.6). Kenttänollan sijaan tehtiin menetelmän ohjeistama "Field train recovery blank" Tämä eroaa kenttänollasta siten, että puhtaan näytelinjan läpi johdetaan typpeä vähintään tunnin ajan. Tämän jälkeen näytelinjasto huuhdellaan samoin, kuin varsinaisen mittauksen jälkeen ja näytteet analysoidaan kappaleessa 2.4.2 kuvatulla tavalla. EPA:n oppaassa "Method 201A and 202 Best Practices to Reduce Blanks, 2015" on ilmoitettu kahden eri laboratorion tyypilliset tulokset "Field train recovery blank" mittaukselle. Toisen laboratorion tulokset ovat tyypillisesti välillä 0.9-1.4 mg ja toisen 1.5 mg. Alla olevassa taulukossa on VTT:n mittaamat tulokset. Tulosten perusteella voidaan todeta, että VTT:llä tehtyjen mittausten "nollataso" on vertailukelpoinen EPA:n oppaassa ilmoitettujen tyypillisten tasojen kanssa. Tulos osoittaa, että VTT:n pesu, näytelinjaston komponenttien käsittely, huuhdonta ja analyysit ovat suoritettu asianmukaisella tavalla ja ilman kontaminaatioita.

Taulukko 4, VTT:n Field Train Recovery Blank -mittausten tulokset

Meas	Inorganic mg	Organic mg	Total mg
1	0.77	0.54	1.32
2	0.43	0.37	0.80
3	0.40	0.42	0.82

Liite 1. Näytetaulukko.

EPA02 Kondensoitunut ja huuhtellussa käytetyt liuotinmäärät, ml												
testinumero:	Testi pvm	Kondensoitunut vesi		Näytelinjaston huuhtelu		Zeflour suodattimen uutto		Vesifaasin uutto ml	Valmis haihdutuk- seen	Yhteensä haihdutukseen		EPA 5
		ml		ml		ml				ml	ml	
		1. impinger	2. impinger	Vesi (2x)	Asetoni (1x) +n-Heksaani (2x)	Vesi 3 x 10	n-Heksaani 3x10	n-heksaani 3x30		Vesifaasi	orgaaninen	asetoni, ml
EPA_202_02	5.6.2017	62	-	51	130	30	30	86	X	140	250	Ei mitattu
EPA_202_03	6.6.2017	63	-	85	90	30	30	87	X	180	200	Ei mitattu
EPA_202_04_FTRB	6.6.2017	Ei mitattu	-	80	100	30	30	87	X	210	220	
EPA_202_05	7.6.2017	65	-	85	100	30	30	86	X	180	200	40
EPA_202_06	7.6.2017	62	-	88	95	30	30	87	X	180	220	40
EPA_202_07	8.6.2017	65	-	85	95	30	30	84	X	180	200	50
EPA_202_08	8.6.2017	67	-	93	85	30	30	85	X	200	200	40
EPA_202_09	12.6.2017	62	-	93	110	30	30	84	X	190	230	40
EPA_202_10	12.6.2017	62	-	100	100	30	30	84	X	190	220	40
EPA_202_11	13.6.2017	58	-	80	100	30	30	85	X	175	230	50
EPA_202_12	14.6.2017	53	-	95	110	30	30	85	X	180	220	40
stin iakeen EPA_202_13	15.6.2017	86	-	100	150	30	30	86	X	200	250	50
EPA_202_14_FTRB	15.6.2017	76	-	80	100	30	30	87	X	190	230	

			5W-30 OIL#1	Shell Mysella SAE40 OIL#2
ENISO12185	Density	kg/m3	851	893.7
ASTMD5771	Cloud point	°C	-13.5	-2.7
ASTMD5950	Pour point	°C	-45	-24
ENISO3104	Viscosity 40°C	mm2/s	70.68	135.3
ENISO3104	Viscosity 100°C	mm2/s	12.04	13.84
ASTMD2270	Viscosity index		168.2	98.2
ENISO20846	Sulfur	mg/kg	2088	>8000
CECL-40-93-B	NOACK	wt-%	8.4	3.5
ASTMD5185	Cadmium	mg/kg	<0,3	<0,3
ASTMD5185	Aluminium	mg/kg	13	12
ASTMD5185	Chromium	mg/kg	0.46	<0,3
ASTMD5185	Copper	mg/kg		<0,2
ASTMD5185	Iron	mg/kg	1.4	0.25
ASTMD5185	Molybdenum	mg/kg	<0,3	<0,3
ASTMD5185	Sodium	mg/kg	27	33
ASTMD5185	Nickel	mg/kg	0.33	<0,2
ASTMD5185	Lead	mg/kg	2.6	<0,3
ASTMD5185	Silicon	mg/kg	3.8	5.1
ASTMD5185	Tin	mg/kg	<0,3	<0,3
ASTMD5185	Vanadium	mg/kg	<0,1	<0,1
ASTMD5185	Barium	mg/kg	<0,3	<0,3
ASTMD5185	Calcium	mg/kg	3100	1400
ASTMD5185	Magnesium	mg/kg	17	3.7
ASTMD5185	Manganese	mg/kg	<0,1	0.15
ASTMD5185	Phosphorous	mg/kg	1000	280
ASTMD5185	Zinc	mg/kg	1200	340
ASTMD874	Sulfated ash	%	1.12	0.47

Workshop / Seminar

Controlling Emissions from Gas Engines

13 November 2018

VTT, Tekniikantie 1, Espoo, room Aari

Program

9.30 *Registration and coffee*

10.00 Opening

Chair Minna Väkevä, Airmodus

10.05 Story of NewGas project

Kati Lehtoranta, VTT

10.20 Main results of NewGas project

VTT - Emissions of natural gas combustion

TUT - Nanoparticles

FMI - Secondary emissions

5 min break

11.15 Case Viikinmäki, Biogas from digestion to engines

HSY - Overview of Viikinmäki wastewater treatment plant

TUT/VTT/FMI - Preliminary results of emission measurements

11.45 Example outside the project scope: Triggers explaining gas vehicle investments in companies

Natalia Saukkonen, TUT Cost Management Center

12.00 *Lunch*

13.15 NewGas industry partners

Joonas Vanhanen, Airmodus

Ville Niemelä, Dekati

Teuvo Maunula/Kauko Kallinen, Dinex Finland

Mika Kettunen, Neste

Joonas Kattelus / Mari Laakso, Oilon

Jan Torrkulla, Wärtsilä

14.30 A word from Business Finland

Pia Salokoski

14:45 Questions and end of the seminar

Coffee and discussion

